

Canadian Journal of Research

-{ Issued by THE NATIONAL RESEARCH COUNCIL of CANADA }-

VOLUME 2

APRIL, 1930

NUMBER 4

THE NEPHELINE SYENITES AND PEGMATITES OF MOUNT ROYAL, MONTREAL, QUE.¹

By F. L. FINLEY²

Abstract

The igneous succession in Mount Royal is outlined emphasizing the fact that there were two distinct advances of a nepheline syenite magma.

Those rocks which are definitely known to belong to the older nepheline syenite and those known to belong to the younger are described separately.

A number of types are described which belong either to the first or to the second intrusion, but whose relations are not definitely known. These include most of the nepheline syenite pegmatites, nordmarkite pegmatites, soda-rich monzonites, syenites and an unusual porphyry intermediate between a shonkinite and an essexite.

Seven chemical analyses are given.

Introductory Note by Frank D. Adams

Mount Royal, around the base of which the City of Montreal has grown, consists of a series of consanguineous igneous rocks of the nepheline syenite-essexite series forming a stock or neck, which is the root of an ancient volcano. It breaks through the nearly horizontal strata of Ordovician age underlying the great plain which forms this portion of the Province of Quebec. The volcano probably came into existence in Carboniferous times. It rises abruptly from the plain to a height of about 800 ft. and constitutes the most westerly of the several similar "mountains" which form the group of the Monteregian Hills.

A series of studies carried out during successive years, by members of the Geological Department of McGill University have made important contributions to our knowledge of the main succession of events in the geological history of the mountain, especially as shown by the surface distribution and relations of the several intrusions. Recently, however, a tunnel has been driven completely through the mountain near its base, by the Canadian Northern Railway (now part of the Canadian National Railway System) to afford ingress to the city of Montreal from the north. This has revealed the inner structure of this ancient volcanic neck, and a detailed study of the geological succession as laid bare in this section was made by Dr. J. Austen Bancroft, at that time Dawson Professor of Geology at McGill University, as the work of driving the tunnel progressed. A series of petrographical studies of the material collected by Dr. Bancroft from the tunnel have been carried out by graduate students in the department of Geology under Dr. Bancroft's close supervision.

The present paper embodies the results of a study of the nepheline syenites which were met with in the tunnel. As the author states, the section cut through the mountain shows that there were at least two intrusions of this rock, instead of one, as was supposed to be the case from a study of the surface exposures, and these important elements in the complex structure of the neck are described in detail. It forms an important contribution to our knowledge of the geology of this interesting mountain.

The paper was submitted as a thesis to fulfil in part the requirements for the degree of Master of Science at McGill University in the year 1924. By Mr. Finley's early decease Canada lost one of her most promising young geologists.

¹ Manuscript received February 22, 1930.

Contribution from the Department of Geology, Faculty of Graduate Studies, McGill University, Montreal.

² Deceased.

Introduction

The volcanic neck or plug which forms Mount Royal presents a complex history of igneous activity. It comprises a varied and interesting group of rocks of plutonic and hypabyssal types, which penetrate gently dipping Ordovician strata.

In common with most of the other Monteregian Hills there were two main intrusions, a basic followed by a more alkaline magma. Dr. F. D. Adams (1,2) first pointed out the relations of these intrusions and described them with their associated dykes. The construction of a tunnel through Mount Royal has offered an unexcelled opportunity for study, and in a recent paper Dr. J. Austen Bancroft and W. V. Howard (5, p. 14-15) have described the igneous succession.

The sequence noted by these authors is as follows:

(1) "By far the major portion of the igneous mass of Mount Royal is composed of essexite which represents the earliest intrusion in the area.

(2) The intrusion of the essexite was followed by a period of dyke injection. The oldest dykes within the area are bostonites, mica-tinguaite and tinguaite-porphyrries, followed by camptonites and monchiquites.

(3) The essexite plug was then shattered and the body of older nepheline-syenite exposed in Corporation Quarry was introduced. At the same time a large number of dykes and dykelets of nepheline syenite traversed the whole body of essexite while a few dykes of nepheline syenite porphyry were injected into the surrounding limestone for distances of at least a few hundred yards from the main igneous mass.

(4) Immediately subsequent to the advance of the older nepheline syenite a vast number of dykes of camptonite, maenaite and other types were injected. Included in this group are dykes of several different ages.

(5) There then followed the extensive intrusion of camptonite that forms the matrix of the igneous breccia which underlies that portion of the second or western summit of Mount Royal beneath which the tunnel passes for over 600 ft. (Stations 246-52 to 253-11). Here the essexite was not only shattered but in places was triturated by the camptonite magma. Fragments of the essexite, of the mica-tinguaite and tinguaite-porphyry of the older nepheline syenite, similar to that exposed in the Corporation Quarry, and also of some of the dykes which were injected after this nepheline syenite, have all been recognized in the camptonite matrix of this breccia.

(6) Numerous dykes of the more recent nepheline syenite varying from a few inches to several feet in width were then injected into the igneous complex of Mount Royal. In some instances these dykes pass from normal nepheline syenite to pegmatitic and aplitic phases, and it is believed that the coarse feldspar dykes, which in many places traverse the essexite, were intruded at this time.

(7) Then followed a closing period of dyke injection which gave rise to at least two types of camptonite dykes of different ages."

Each period of intrusion was followed by one of cooling and solidification, and the above sequence provides a complex example of differentiation. This is especially striking where the two ages of nepheline syenite are separated by an extremely basic camptonite, as illustrated by the matrix of the breccia.

The present paper is the result of a petrographical study of the nepheline syenites and the allied soda-rich rocks of the area, included in group 3 and group 6.

Mineralogical Composition

Before describing these rocks an enumeration and short description of the minerals composing them will be given. The following have been observed:

PRIMARY

Orthoclase	Biotite	Fluorite
Plagioclase	Lepidomelane	Corundum
Nepheline	Muscovite	Pleonaste
Hornblende	Sphene	Astrophyllite
Aenigmatite	Garnet	Apatite
Augite	Zircon	Pyrite
Aegerine-augite	Nosean	Pyrrhotite
Aegerine	Sodalite	Black Iron Ore
Wollastonite		Calcite

SECONDARY*

Kaolin	Natrolite	Rutile
Calcite	Sodalite	Selenite
Sericite	Analcite	Pyrite
Giesekite	Hydronephelite	Hematite and Limonite
Cancrinite	Chlorite	Quartz
	Leucoxene	

Within the highly altered Trenton limestone, adjacent to some of the dykes that have been studied, the following minerals were present:

Calcite	Aegerine-augite	Orthoclase
Garnet	Augite	Plagioclase
Vesuvianite	Wollastonite	Nepheline
Diopside	White mica	Pyrite

Feldspars

Orthoclase is the dominant feldspar in these rocks. It shows the ordinary characteristics, and has usually a strong tendency to elongation parallel to the clinopinacoid. The color ranges from pale grey to pale salmon pink. Though the most prominent feldspar, it is invariably associated with plagioclase under more or less intimate conditions. Microperthitic intergrowths are very com-

*Some of these minerals at least are not secondary in the sense of having been produced by later processes of weathering or decay but were deposited from waters given off by the cooling magma in the final stages of volcanic activity.

mon and anorthoclase is abundant, especially in many of the aplitic and pegmatitic phases. By refractive index and extinction angle determinations the plagioclase has been found to range from practically pure albite to $Ab_1 An_1$, or intermediate oligoclase. In one unusual case which will be discussed later, the interior of zoned phenocrysts approaches labradorite, approximately $Ab_1 An_1$. The plagioclase usually develops somewhat better crystal outlines than the orthoclase and can be readily identified in the hand specimen by its blade or lath-like character. Albite and Carlsbad twinning are very common and pericline is not unusual. Mannebach is very unusual and has only been observed in one or two cases. Microcline is of rare occurrence.

Though the feldspars in samples taken from the tunnel are remarkably fresh, incipient alteration to kaolin, sericite and finely disseminated carbonate are frequently encountered. Near the surface alteration is further advanced although in some localities remarkably fresh examples can be obtained.

Nepheline

As Dr. Adams (2, p. 40) has pointed out, this mineral is so abundant that the rock gelatinizes readily when powdered and heated with dilute hydrochloric acid. The relative amount however is somewhat variable, and its greatest development is seen in some of the aplites and pegmatites. Its color is usually a dull grey with a greasy lustre, and less commonly it is flesh tinted and vitreous to greasy. The flesh tint is in part due to incipient alterations but perfectly fresh examples have been examined which also show this color. By far the most common decomposition product is cancrinite, which has only been found as a secondary product. Sericite, sodalite, hydronephelite, analcite and a pale brown scaly mica, probably giesseckite (12) are others. Analyses (9) of the pinkish unaltered nepheline and of the analcite are given below.

TABLE I
ANALYSES

	Nepheline	Analcite
SiO ₂	44.98%	54.83%
Al ₂ O ₃	32.65	24.20
Fe ₂ O ₃	0.72	
CaO	trace	0.08
MgO		
Na ₂ O	16.08	12.01
K ₂ O	4.54	
H ₂ O	0.97	8.50
Total	99.94	99.62

Amphiboles

The typical hornblende of these rocks shows fair crystal form, usually in elongated narrow prisms, although stouter prisms are also seen. The color is very deep green or black. In thin sections the interior is often brownish while the margin is deep green. Opacite rims with the separation of dust-like particles of magnetite, are common features. Pleochroism is fairly strong.

A hornblende presenting somewhat different characteristics is met with in a number of the dykes. Optically it is negative and the pleochroism ranges from X=yellowish green to Y=Z=deep bluish green. The axial angle is small, and the maximum extinction angle is 28° . A closer determination could not be made but the properties suggest hastingsite.

In several thin sections, a few small prismatic grains of a mineral are found which has been identified as aenigmatite. It possesses a good cleavage and an extinction angle of about 3° . The pleochroism is intense, brown-black to clear red-brown.

Pyroxenes

In thin sections the augite of these rocks may be almost colorless, or purplish and faintly pleochroic. More commonly it is very pale green with slight absorption. Aegerine-augite with similar characteristics and deep green, slightly pleochroic aegerine are also present, the latter being confined to the pegmatites. An analysis of the aegerine (9) is given below.

TABLE II
ANALYSIS OF AEGERINE

	Per cent		Per cent
SiO ₂	49.51	MgO	1.09
TiO ₂	0.61	CaO	7.16
Al ₂ O ₃	2.72	Na ₂ O	8.62
Fe ₂ O ₃	22.26	K ₂ O	0.38
FeO	5.82	H ₂ O	0.57
MnO	1.51		
		Total	100.25

Where some of the pegmatites cut limestone, much lime has been absorbed. This has combined with silica to form wollastonite. Though its source is undoubtedly extraneous to the magma it has crystallized from solution with the other constituents and in this sense must be regarded as primary. The crystals show good prismatic outlines, elongated parallel to the b axis, and the usual twinning and cleavages. The mineral also forms an important constituent of the contact metamorphic zone.

Micas

The micas, lepidomelane and biotite, are deep green or brown in color, and both are intensely pleochroic. Though generally very subordinate in amount to hornblende, the mica assumes a position of importance in some of the dykes. In a few instances it occurs to the exclusion of the hornblende. Primary white mica, probably muscovite is rare. The composition of lepidomelane from a pegmatite in the Corporation Quarry is given in Table III.

TABLE III
ANALYSIS OF LEPIDOMELANE (9)

	Per cent		Per cent
SiO ₂	32.96	MgO	0.73
TiO ₂	2.80	Na ₂ O	0.98
Al ₂ O ₃	10.34	K ₂ O	7.75
Fe ₂ O ₃	8.85	Li ₂ O	0.03
FeO	27.19	F	none
MnO	2.79	H ₂ O	4.36
CaO	0.64		
		Total	99.42

Sphene

This mineral appears in all of these rocks. It is especially plentiful where the content of hornblende is high. Colorless crystals are most common, pale brown are rather rare, and in only one case was a strongly pleochroic example seen, varying from yellowish green to deep reddish brown. Alterations to calcite, opaque iron oxide, and calcite with reticulated groups of rutile needles are frequent.

Garnet

Though not invariably present, garnet is a very common accessory. The crystal habit is the dodecahedron though in one pegmatite, octahedral forms are abundant. Irregular shapes ranging up to two or even three millimetres in diameter are the general rule. The color ranges from brown, through deep red-brown to black (melanite). Under the microscope lighter shades of brown are seen and a concentric zonal arrangement is at times developed. Minute inclusions of sphene, nosean, magnetite and plagioclase are often abundant. In one case an internal intergrowth or replacement by fluorite was observed in a relatively large dodecahedral crystal. Optical anomalies are infrequent.

Zircon

Though rarely of more than microscopic proportions, zircon is a very common accessory. In one of the pegmatites, however, crystals up to one and a half millimetres in size were observed. These had a pale yellow color and were in bipyramidal forms. In thin sections it is colorless but in a few cases it is of a very pale brown shade. Slight variations of this tint produce a concentric zonal banding. This is particularly noticeable between crossed nicols when each successive zone is marked by a different interference color.

Nosean

Commonly confined to volcanic types this mineral is very abundant in some of these rocks. In thin sections it is colorless and shows rounded or hexagonal outlines. It is invariably filled with minute opaque inclusions which usually show a tendency to concentrate towards the centre of the crystals, but which are also concentrically or irregularly distributed. A zonal structure is sometimes seen.

Sodalite

Several relationships have been observed in the case of this mineral. It ordinarily occurs as rounded or irregular grains, sometimes with a tendency to hexagonal outlines, forming a normal constituent of the rock. It is thus particularly well developed in the pegmatites. As a decomposition product of the nepheline it has already been mentioned. In one of the aplites it is found both as a normal constituent and as a filling of minute fissures. In this last case, movement evidently took place after almost complete solidification. The margin of the dyke, which is somewhat more basic than the interior, has been strongly sheared and in the closely spaced parallel fissures, sodalite and abundant pyrite have been deposited. Towards the center of the dyke the minute cracks are very irregular and curving but are similarly filled. The sodalite was probably deposited by pneumatolytic agencies and the irregular character of the interior cracks is interpreted as evidence of partial plasticity.

Because of its pale azure blue color this mineral may be readily distinguished in the hand specimen. An analysis by Dr. Harrington (8) shows it to possess the following composition:

TABLE IV
ANALYSIS OF SODALITE

	Per cent		Per cent
SiO ₂	37.52	Na ₂ O	19.12
Al ₂ O ₃	31.38	K ₂ O	0.78
Fe ₂ O ₃	trace	{Na	4.48
CaO	0.35	{Cl	6.91
MgO	trace	Total	100.54

Fluorite

Deep purple fluorite is not of frequent occurrence though in some of the pegmatites it is rather abundant. In thin sections it invariably presents anhedral forms, and though generally colorless it sometimes shows patches of a deep bluish violet color.

Corundum

This mineral was identified in a hand specimen taken from a dyke of the later nepheline syenite (Tunnel Station 251+66). It occurs as grains and crystals so small that they can only be distinguished under the microscope, constituting nevertheless almost 5% of the rock. A few hexagonal and tapering sections are seen but anhedral grains are far commoner. It is colorless but in some cases shows irregularly distributed zones which are distinctly blue and pleochroic, bluish to colorless. Optically it is uniaxial and negative.

Corundum has not been previously identified on Mount Royal or in fact within the Montereian petrographical province. It is then of special interest to find that even so local a portion of the magma as a single dyke

was supersaturated with alumina. A further point of interest is attached in that the appearance of this mineral connects these rocks, petrographically at least, with the far more spectacular development of corundum syenites in the Haliburton and Bancroft areas of southeastern Ontario (4, 10).

Pleonaste

The occurrence of this mineral is restricted to a dyke of later nepheline syenite porphyry, 0.5 in. in width, (Tunnel Station 246+25) within which it is disseminated as abundant small irregular grains.

Astrophyllite

Small grains of a mineral showing the characteristic cleavage and pleochroism of astrophyllite have been observed embedded in fluorite.

Calcite, etc.

In samples of dykes taken from the very core of the mountain, and unaltered in every respect, calcite is found in clear interstitial forms. Such occurrences force the conclusion that it is primary.

Apatite, pyrrhotite and black iron ore present their usual characteristics, and occur as minor accessories. The last is frequently titaniferous and is partially decomposed to leucoxene.

Further mention of the secondary minerals does not seem necessary at this point. The occurrence of gypsum in drusy pegmatites is of especial interest and will be discussed later.

The contact metamorphic zones have been described in a previous paper (7), and nothing can be added as to the characteristics of the minerals or their paragenesis. It is noticeable, however, that the normal nepheline syenite dykes have little effect on the limestone while even the smallest of the pegmatites produce very pronounced contact metamorphic effects.

Occurrence and Characteristics

THE OLDER NEPHELINE SYENITE

The main intrusion of nepheline syenite occurs on the northwest slopes of the mountain. It is irregular in outline and occupies an area of about half a square mile. Good exposures are abundant, and the almost vertical contact with the Trenton limestone to the north is well exposed in the Corporation Quarry. Along the southern contact, where the rock intrudes Essexite, a breccia is frequently developed, the matrix of which is the normal nepheline syenite, and the inclusions are commonly of the pyroxenite phase of the Essexite (5). Fragments of every size are seen from large blocks several feet in diameter to broken fragments of crystals. This breccia is excellently exposed in the vicinity of the small pond in the Roman Catholic Cemetery, where the rock exposures are smooth and polished by glacial action and the thin mantle of drift has only recently been removed. Here the fragments occupy more space than the matrix, and both are cut by small stringers of nepheline syenite aplite, which in turn are traversed by camptonite dykes.

The older nepheline syenite shows remarkably little variation. It is grey or more rarely pinkish in color, medium-grained, and possesses a hypidiomorphic texture. It is composed essentially of orthoclase, nepheline and hornblende with albite, augite, aegerine augite, biotite, sphene, garnet, zircon, sodalite and other minerals as accessories. Nosean is a characteristically abundant accessory and though it is sometimes found in the younger nepheline syenite it is never so plentiful. A porphyritic appearance is occasionally developed due to the presence of larger hornblende and augite crystals having maximum dimensions of about a centimetre. This phase may be seen 400 ft. east of the Corporation Quarry. At some of the contacts a tendency to flow structure is observed, as evidenced by the horizontal alignment of the individual grains.

On the only detailed map (2)* of the area seven other small bodies are shown. In some cases these represent areas in which there are very numerous dykes of nepheline syenite, and in which the mapping has been somewhat generalized. These show such a similar composition and appearance to the main mass that they are believed to have been intruded at the same time. The three small masses outcropping near the "Lookout", in the vicinity of the baked collar of Utica shale, are so deeply decomposed that no definite determination can be made.

In the construction of the tunnel numerous dykes of nepheline syenite were encountered. Where these, through intersections with dykes of known age, can be definitely assigned to the older nepheline syenite they show characteristics identical to it, although usually somewhat finer grained. To this only two exceptions have been noted. In a few dykes albite assumes a position of equal or greater importance than orthoclase, though no other points of difference arise. Finally, to the north of the main nepheline syenite mass, at least four dykes of nepheline syenite porphyry have been injected into the limestone for distances of several hundred yards or more. Their outcrop has not been discovered, and they are exposed only in the tunnel. These porphyries are a little darker grey than the normal nepheline syenite and contain more abundant nosean than has been observed in any other type. The phenocrysts are prominent, up to four millimetres in diameter, and consist of plagioclase, orthoclase and nepheline, the plagioclase being zoned from intermediate oligoclase to albite. The dark minerals show poorer idiomorphic outlines and include augite, hornblende and biotite, together making up from one-eighth to one-fifth of the rock. These are set in a fine-grained groundmass consisting of irregularly disposed small laths of orthoclase and albite with abundant interstitial nepheline. Sphene, magnetite, pyrite, apatite and in one case melanite, are accessories.

*Mapping by J. J. Stansfield.

THE YOUNGER NEPHELINE SYENITES

Previous to the construction of the tunnel a second distinct advance of the nepheline syenite magma had not been recognised. It is true that aplitic and pegmatitic dykes (2, p. 45) had been commented upon but these were merely considered to mark the final phase of a single period. As the heading advanced into the camptonite breccia, however, incontrovertible evidence became available that this was not the case. The breccia contains besides fragments of other older rocks, abundant inclusions of older nepheline syenite. These are identical with the nepheline syenite of the main mass, from which they were undoubtedly derived, and vary in size from large blocks to minutely triturated grains. The breccia with its included fragments of the older nepheline syenite, is traversed by numerous dykes and abundant dykelets of a younger nepheline syenite. The small monzonite stock of Mount Royal Heights, which though of similar character and relationships, has been modified by its absorption of siliceous and calcareous inclusions, can probably be assigned to this period (11).

Mineralogically, the typical younger nepheline syenite shows little or no difference from the older, and indeed it is difficult to give a description which would serve as an infallible guide in distinguishing the two. To the trained observer in this area there are, however, certain features upon which a classification can be made with some degree of certainty, even where field relations are obscure. It is somewhat finer grained than even the older nepheline syenite dykes, and distinctly finer grained than the main intrusion. Moreover it is usually a little lighter grey in color. The most characteristic feature which it exhibits is a strong tendency to differentiate towards aplitic and pegmatitic types, and it is also represented by homogeneous aplites and pegmatites. In those types intermediate between the aplite and the nepheline syenite, biotite is apt to be the dominant dark mineral, and in some cases completely displaces hornblende.

The aplites are found in profusion cutting the camptonite breccia. The typical variety is pinkish in color, medium-grained and distinctly granular. In thin section it is seen to be almost entirely composed of orthoclase, nepheline and plagioclase, in decreasing order of importance, all of which are at times intergrown. In addition there are a very few and usually small fragmentary individual grains of strongly pleochroic hornblende, a few ragged individuals or aggregates of small flakes of biotite, one or two irregular dusty grains of nosean, and widely disseminated small grains of magnetite, pyrite and sphene. Occasionally melanite, aegerine-augite or augite, sodalite and fluorite may be present.

These aplites are by no means confined to the breccia, but have been intersected elsewhere in the tunnel and are also well exposed, cutting the older nepheline syenite in the vicinity of the Corporation Quarry. In this last case they could possibly be assigned to the final period of consolidation of the older intrusion, were it not for the following significant facts. Similar petro-

graphical types are known to cut the camptonite breccia and to be closely associated with the younger nepheline syenite. They are in no sense aplitic segregations of the main mass, such as are so often found in large areas of granitic rocks, but occur in well defined dykes cutting it. Finally though fragments of the older nepheline syenite are so abundant in the camptonite breccia, no aplite fragments have been found.

Though many of the aplites show a tendency towards pegmatitic phases, especially in the Corporation Quarry, only one sample of a pegmatite has been examined which cuts the camptonite breccia and is therefore definitely to be assigned to the younger nepheline syenite (Tunnel Station 252+84).

A number of smaller occurrences, however, are recorded in the field notes, emphasizing similar characteristics. This rock is coarse grained, with crystals having diameters up to one-half inch, and is composed almost entirely of feldspar and nepheline, in about equal amounts, together with a very few rather large flakes of black mica and rather abundant purple grains of fluorite. A number of drusy cavities are present, and in these calcite has been deposited together with projecting acicular crystals of natrolite. The rock has a curious mottled appearance due to the sharp contrast of the white feldspar and the flesh-colored nepheline. In the thin section a very few small sphenes and minute zircons are observed, and the feldspar is seen to be albite with subordinate orthoclase. In the interstices between some of the larger feldspar crystals or gathered in small groups in the nepheline are found small, irregularly disposed albite laths. The mica is intensely pleochroic lepidomelane, somewhat altered around its margin and along cleavage cracks to little grains of magnetite. Finely disseminated pyrite and a little secondary cancrinite and sericite are present. The twinning laminae of the albite are bent in many cases and strain shadows are prominent. Evidently the rock has undergone considerable pressure though no cataclastic structure has developed.

Of rock types which are definitely known to represent the younger nepheline syenite, only the porphyries remain. These are almost as restricted in their occurrence as those belonging to the older period. They show, however, more diversity than the older nepheline syenite porphyries, reflecting the strong tendency of the second intrusion to differentiate into somewhat varied types.

The most prominently porphyritic dyke cuts the camptonite breccia at Tunnel Station 248+83, and in the hand specimen greatly resembles the older porphyries. In thin sections however, several points of difference arise. Nosean is completely absent instead of being abundant, the groundmass is granular rather than lath-like, and orthoclase does not occur in phenocrysts. The most pronounced phenocrysts are tabular crystals of nepheline, in some cases showing the characteristic overlapping or shingle structure and subordinate to these are plagioclase crystals zoned from intermediate oligoclase to albite. Prisms of hornblende are rather abundant and are largely altered to pale green chlorite with the separation of little grains of pyrite. Pale green augite, fringed or altered along cracks to a similar chlorite, is a lesser

constituent. There are a number of small altered sphenes, and the granular groundmass is composed of orthoclase, abundant nepheline and a little albite. Through this are disseminated grains of pyrite, a little magnetite, and much sericite, finely diffused calcite, and secondary cancrinite.

A somewhat more acidic and finer grained phase is found at Tunnel Station 246+25. Here the breccia is cut by innumerable irregular little dykes and stringers. In thin section one of these was found to contain phenocrysts of orthoclase and oligoclase, in about equal proportions, and very small disseminated flakes of strongly pleochroic brown biotite. These are set in a fine-grained, granular groundmass of orthoclase and nepheline. Irregular grains of pleonaste, a few minute zircons and rounded grains of magnetite and pyrite are accessories. Small irregular areas of calcite, a little sericite and a few small radiating groups of needle-like crystals of natrolite are present as decomposition products. The rock is very pale grey in color and the phenocrysts attain a fairly uniform length of about two millimetres.

In a few cases thin sections reveal a tendency to porphyritic structure which is not observable in hand specimens. This is well illustrated in a sample from Tunnel Station 252+71. The rock is characterized by very abundant grains of nepheline together with those of orthoclase and albite. All three are equigranular, exhibit a tendency to idiomorphic outlines, and are, in part, micrographically intergrown. In the interstices between them are closely packed small hypidiomorphic grains of the same minerals. Biotite, in small flakes or in aggregates of small flakes, is sparsely disseminated through the rock. Zircon, sphene, a little dusty nosean, a very little sodalite, one or two anhedral grains of fluorite and disseminated grains of pyrite and magnetite are accessories. It is a nepheline syenite very low in mafic constituents.

THE TWO INTRUSIONS OF NEPHELINE SYENITE

The presentation of the above facts can leave no doubt as to the advance of two distinct nepheline syenite magmas, and their existence and recognition is probably the most important contribution of this paper. The first and major intrusion is a nepheline syenite of generally uniform character with relatively few textural or mineralogical variations, while the second, though in some cases very similar, is largely represented by less mafic types. Together with the intervening basic intrusion of camptonite they add still further to the already complex problems of differentiation in the area.

Regarded broadly the Monteregian Hills show major basic intrusions followed by more acidic alkalic magmas. The repeated pulsation from basic to acidic magmas is illustrated by Mount Royal. It is not the purpose here to discuss this differentiation, which is a problem falling outside of the scope of this paper. It is desired however to emphasize the fact that the igneous sequence in Mount Royal does not illustrate increasing acidity, but rather successive advances of basic magma, each followed in turn by an advance of acidic magma.

TYPES WHICH MAY BELONG TO EITHER FIRST OR SECOND PERIOD

A number of distinct rock types have been examined whose age is not made evident by field relations. These are undoubtedly to be assigned either to the older or the younger nepheline syenite, and in some cases indirect evidence favors their association with one or the other. It seems preferable however to describe them separately pending more definite information.

Pegmatites

Foremost amongst these are the pegmatites found between the main essexite contact and Tunnel Station 191+33. They intersect uncorrelated camptonite dykes and are intruded into Trenton limestone. The grain is coarse, individual crystals attaining diameters, of two cm. or more with an average of about one cm. and the color is white or pale grey. Exclusive of nosean, pleonaste and corundum, all the minerals previously mentioned and described are at times present. Orthoclase and nepheline are essential constituents and the former nearly always shows micropertthitic intergrowths. Albite is invariably present in long narrow prisms, anorthoclase is of very general occurrence and occasionally graphic intergrowths between albite and orthoclase are seen. Lepidomelane, hornblende and the pyroxenes may be sparsely distributed or may be completely absent. Fluorite and sodalite, though not invariably present, here reach their greatest development, and melanite may be locally abundant. With the exception of sphene and zircon, other accessory minerals are not much in evidence. The proportion of nepheline present varies greatly in different dykes, this mineral usually being of a dull grey color, more rarely, of a pinkish tint.

These nepheline syenite pegmatites form well defined dykes up to eight inches in width and also occur as irregular dyke-like injections. In one case (Tunnel Station 194+50) a granular nepheline syenite dyke is braided with irregular pegmatitic segregations. The nepheline syenite is of the normal type except that the mafic constituents are represented only by aegerine augite intergrown with an occasional flake of biotite.

The contact metamorphic effects upon the limestone have already been mentioned and in addition fragments of limestone are sometimes included giving rise to beautiful crystals of vesuvianite. In one instance (Tunnel Station 193+35) the pegmatite is literally banded with inclusions of white crystalline limestone holding a few vesuvianite crystals. On being struck with a hammer it gives off a most unpleasant stench not unlike that of the old fashioned sulphur match. When examined under the microscope the individual calcite grains are often seen to contain little brownish patches of a material which is believed to be of organic origin, and to it the stench is attributed.

Nordmarkite Pegmatites

A number of coarse feldspar pegmatites cut the essexite as dykes attaining a width of three or four feet. More often however, they are extremely irregular, pinching and swelling and following tortuous courses through the essexite. A somewhat similar association with nepheline syenite pegmatites has been noted in eastern Ontario (3).

These pegmatites are coarse-grained rocks, the feldspar often attaining diameters of one inch or more. Drusy cavities are abundant. In color, they vary from a pale to a deep salmon pink. Coarse interlocking crystals of orthoclase form the greater part of the rock, and dull green earthy masses of chloritic material with calcite represent some allied ferro-magnesian constituent which was present in subordinate amount. With the microscope, remnants of biotite or augite together with an occasional highly altered sphene and a little black iron ore can be detected. The orthoclase is perthitically intergrown, an orthoclase is present, and a few small prismatic crystals of albite are included in the larger individuals of orthoclase. Into the cavities, orthoclase crystals have grown freely and are coated, and in part replaced, with quartz, calcite, gypsum and pyrite. Acicular crystals of natrolite project into the cavities and this mineral often forms more massive incrustations. The gypsum is of the variety selenite and is frequently found in large crystals three or four inches across. It is colorless and transparent and is associated with quartz and with coarsely crystalline, yellowish or pale blue calcite. Some doubt is felt as to the origin of the gypsum. The present underground waters are of a dominantly sodium carbonate type, though within certain restricted areas calcium sulphate and other saline waters occur. C. L. Cumming considers that the salts possibly originated at the time of the volcanic eruption of Mount Royal (6). It seems probable that the gypsum was formed through the agency of acid volcanic waters directly connected with these dykes, for it is significant that gypsum is not found with other rocks of the area. It might be pointed out that the drusy character of these pegmatites lends itself to the circulation of solutions of meteoric origin. On the other hand equally porous nepheline syenite pegmatites and the shattered rocks of the contact are completely barren of selenite.

This rock has been classified as a nordmarkite pegmatite. A complete analysis (Analysis D Table VI) has been made. For purposes of comparison a partial analysis of this rock is here shown with those of two others of nordmarkite from different localities.

TABLE V
ANALYSES OF NORDMARKITES

	I Per cent	II Per cent	III Per cent
SiO ₂	63.20	61.77	68.04
Al ₂ O ₃	18.94	18.05	17.92
Fe ₂ O ₃	0.27	1.77	0.96
FeO	1.00	1.75	2.08
MgO	0.38	0.89	0.59
CaO	1.50	1.54	1.00
Na ₂ O	5.84	6.83	6.67
K ₂ O	7.56	5.21	6.08
H ₂ O	0.11	1.10	1.18

NOTE:— I. Nordmarkite pegmatite, Montreal, Que. M. F. Connor.
 II. Nordmarkite, Brome Mountain, Que.
 III. Nordmarkite, Tonsenas, near Christiana, Norway.

A feature observed in a number of these dykes is a marginal phase of very different composition and texture. It is a rock of medium grain, equigranular and dark grey in color. Examined in thin section it is found to consist of tabular crystals of orthoclase and oligoclase in about equal proportions, abundant elongated and often irregular prisms of hornblende with green margins and brown interiors, prisms or irregular forms of pale green augite, and a few flakes of biotite intergrown with the hornblende. Abundant sphene, titaniferous iron ore and apatite are present as accessories. The rock is very fresh but a little finely diffused calcite and sericite are present. It has been classed as an alkali-monzonite.

Though small stringers of the nordmarkite pegmatite interior cut the monzonite margin, the phenomenon can in no sense be interpreted as the intrusion of a younger dyke along the line of weakness in the older. Rather it indicates an excess of mineralizers and an acidifying of the magma either through marginal segregation or through differentiation at depth. The latter case seems the most probable in view of the sharp contacts between the two types.

Soda-rich Monzonite

A somewhat similar soda-rich monzonite is found at Tunnel Station 229+05 where it forms a well defined dyke three feet wide. It is medium-grained and on first appearance it very much resembles the older nepheline syenite, though darker grey in color. Upon a microscopic examination however nepheline is found to be completely absent, the feldspar consists of oligoclase and orthoclase, the former in excess of the latter, and abundant biotite and pale green augite which are in part intergrown. Sphene, apatite, titaniferous iron ore and pyrite are accessories and minute zircons are present in more than usual proportions.

Syenites

The dykes, at Tunnel Station 208+66 (Analysis G Table VI) and 195+38.5, are syenites. Both of these dykes are highly altered; in the first mentioned the dark mineral has been completely replaced by calcite and a dull green chloritic material, and in the second only a few shreds of biotite remain. Both are pink in color, medium-grained and possess hypidiomorphic structure. In thin sections, albite and orthoclase appear in about equal proportions. Microperthitic intergrowths are common, and in a few individuals a micrographic intergrowth appears. Sphene, zircon, and titaniferous iron ore and apatite are accessories. The feldspar is fairly fresh but shows some alteration to calcite and kaolin together with a little staining with hematite.

Shonkinite Porphyry

An interesting porphyritic dyke, 30 in. wide, occurs at Tunnel Station 254+06 (Analysis F, Table VI) in the vicinity of the older nepheline syenite porphyries. It is grey in color and contains prominent phenocrysts of black hornblende and augite up to 0.5 in. long. Feldspar phenocrysts though abundant are somewhat less prominent. In the finer grained groundmass the same minerals can be distinguished. It holds a number of inclusions of essexite.

In thin sections, the hornblende is pleochroic from yellowish green to deep green while some crystals show brown interiors and green margins. The augite is very pale green or almost colorless often with slightly greener margins. Both some of the hornblendes and some of the augites show incipient alteration to calcite, chlorite and a little iron ore dust, the latter especially in the case of the hornblendes. The abundant phenocrysts of plagioclase are zoned from acid labradorite, at the centre, to intermediate oligoclase. Numerous grains, or wedge-shaped crystals, of sphene are present often showing alterations to calcite and to grains of black iron ore around their margins. Dusty nosean often showing idiomorphic outlines is particularly abundant and is often poikilitically enclosed in the larger augite and hornblende phenocrysts. One large individual of augite contains 42 small rounded grains of nosean. Quite large grains of titaniferous iron ore and pyrite are distributed through the rock and prisms of apatite are quite abundant, especially in the hornblende and augite phenocrysts, or enclosed in the larger grains of iron ore. The ground-mass consists of little irregularly disposed laths of albite-oligoclase with slightly subordinate grains of orthoclase and a fair number of grains of nepheline. Scattered through this are minor grains of iron ore and pyrite with much diffused calcite and a little sericite.

Some difficulty has been experienced in correctly naming this rock, for it is in reality a type intermediate between essexite and shonkinite. The character of the feldspar separates it from the shonkinites, and yet the rock hardly seems calcic enough or rich enough in dark constituents to be termed an essexite. Chemically it is most closely allied to the shonkinites and rather than add to an already voluminous nomenclature it has been called shonkinite-porphyry, keeping in mind the above reservations.

Analyses

Seven analyses are given of the various rocks described, and with one exception these have not been published previously. All of these analyses were made by M. F. Connor of the Geological Survey of Canada. In the calculation of the norm of the nordmarkite pegmatite it was necessary to form 0.34% of magnesium carbonate, as sufficient lime is not present to balance the carbon dioxide. The norm for the altered pink syenite has not been calculated as there is a considerable deficiency of lime, necessary to form calcite, and an adjustment as in the last case is not deemed advisable.

TABLE VI
SPECIMENS ANALYZED

	A	B	C	D	E	F	G
SiO ₂	55.90	56.28	56.30	63.20	53.84	49.84	58.20
Al ₂ O ₃	19.75	22.53	20.96	18.94	19.68	19.46	17.57
Fe ₂ O ₃	1.00	1.14	2.04	0.27	2.64	2.67	1.94
FeO	2.05	0.90	1.58	1.00	4.37	2.82	1.43
MgO	0.59	0.23	0.49	0.38	2.06	1.55	0.78
CaO	3.10	1.50	3.28	1.50	6.60	6.06	3.77
Na ₂ O	7.25	10.25	6.57	5.84	6.24	8.04	6.14
K ₂ O	5.61	5.46	5.69	7.56	2.10	3.18	4.80
H ₂ O	2.00	0.90	1.40	0.11	0.25	1.45	0.74
CO ₂	1.85	0.45	0.31	1.30	trace	2.03	3.48
TiO ₂	0.70	0.25	0.60	0.10	1.50	1.54	0.36
P ₂ O ₅	0.01	0.06	0.09	0.10	0.36	0.42	0.18
SO ₃	0.04	0.20	0.20	0.14	0.26	0.40	0.11
Cl	trace	0.09	0.17	0.14	0.19	0.15	0.10
FeS ₂			0.30	0.04		0.17	0.12
Fe ₇ S ₈			0.01	0.02			
MnO	0.10	0.13	0.09	0.03	0.12	0.20	0.05
SrO	trace		0.04	0.04			0.07
BaO	0.09		0.21	0.05			0.21
S	0.64	0.27			0.15		
Cr ₂ O ₃						none	
NiO						none	
Total	100.68	100.64	100.33	100.76	100.32	99.98	100.05
Locality	Older Nepheline syenite in the Corporation Quarry	Younger Nepheline syenite. Mount Royal Tun- nel Sta. 252+71.	Younger Nepheline syenite. Mount Royal Tun- nel Sta. 252+50	Mount Royal Tun- nel Sta. 197+58	Mount Royal Tun- nel Sta. 229+05	Mount Royal Tun- nel Sta. 254+06	Mount Royal Tun- nel Sta. 208+66
Name	Nepheline syenite	Nepheline syenite	Nepheline syenite	Nordmarkite pegmatite	Soda-rich monzonite	Shonkinite porphyry	Syenite
Symbol	1.(5)6.1".#4.	I.6.1.4.	1".5'.2.(3)4.	I.5.1.3.	II.5.(2)3.4'.	(I)II.6.2.4.	
Classifi- cation	Persalane Russare Miaskose Miaskose	Persalane Russare Miaskose Miaskose	Persalane Canadare Pulaskose	Persalane Canadare Normarkase Phlegrose	Dosolane Germanare Andase Andose	Dosolane Norgare Essexase Essexose	Not calcd. due to alteration

TABLE VII

NORMS OF ROCKS ANALYSED

	A	B	C	D	E	F	G*
Orthoclase	33.36	32.25	33.92	44.48	12.23	18.90	
Albite	39.30	31.44	35.63	47.16	42.44	35.11	
Anorthite	4.17	0.28	12.79		21.13	10.29	
Nepheline	11.93	28.97	8.52	0.57	4.83	15.34	
Corundum	0.10			1.53			
Halite			0.59	0.23	0.35	0.23	
Thenardite		0.43	0.43			0.71	
Diopside		1.30	0.88		7.94	3.52	
Hypersthene				1.95			
Olivine	1.56		0.83		3.39	2.09	
Wollastonite		1.16					
Magnetite	1.39	1.62	3.02	0.46	3.71	3.94	
Ilmenite	1.37	0.46	1.22	0.15	2.89	2.89	
Pyrite	1.20	0.48	0.30	0.04	0.24	0.17	
Pyrrhotite			0.01	0.02			
Apatite			0.34	0.34	0.67	1.01	

*G. Not calculated owing to alteration.

Acknowledgments

The writer is greatly indebted to Dr. J. A. Bancroft for aid in the investigation and for helpful criticism in the preparation of this paper. By far the greater number of the specimens examined were placed at his disposal by Dr. Bancroft, who collected them during the construction of the tunnel. Sincere thanks are also due to Prof. R. P. D. Graham and Dr. J. J. O'Neill for many valuable suggestions.

References

- ADAMS, F. D. J. Geol. 11:239-282. 1903.
- ADAMS, F. D. Guide Book No. 3, 12th International Congress 1913.
- ADAMS, F. D. and BARLOW, A. E. Trans. Roy. Soc. Can. [IV] 2: 3-76. 1908.
- ADAMS, F. D. and BARLOW, A. E. Geology of the Haliburton and Bancroft Areas, Ontario, Mem. 6. Geol. Survey Can. 1910.
- BANCROFT, J. A. and HOWARD, W. V. Trans. Roy. Soc. Can. (3) XVII:13-14. 1923.
- CUMMING, C. L. The Artesian Wells of Montreal. Mem. 72. Geol. Survey of Can. 1915. p. 5-11.
- DOLAN, E. P. Trans. Roy. Soc. Can. (3) XVII: 127-151. 1923.
- HARRINGTON, B. J. Notes on a few Canadian Minerals—(Extract from the Report of the Geol. Survey Can. 1874-5).
- HARRINGTON, B. J. Trans. Roy. Soc. Can.
- MILLER, W. G. Report Bureau of Mines, Toronto, Vol. 8, part 2. 1899.
- PELLETIER, R. A. Absorption of Inclusions of Potsdam sandstone by an Alkalic Magma. Mount Royal Heights, Montreal, 1924. (Unpublished).
- ROSENBUSCH, H. Mikroskopische Physiographie, p. 113.

THE SPECIFIC EFFECTS OF MONOCHROMATIC LIGHT ON THE GROWTH OF YEAST¹

BY A. H. HUTCHINSON² AND DOROTHY NEWTON³

Abstract

An isolated strain of *Yeast*, derived from Fleischman's preparation, when exposed to monochromatic light responds quite differently to light of different wave-lengths. Slight retardation in growth by red and orange light, stimulation by yellow and green, and increasingly marked retardation in the blue and violet, characterize the effects of the mercury lines of the visible spectrum. There is a sudden transition to stimulation in the near ultra-violet. (λ 3984 Å). Stimulation continues at λ 3650 Å and characterises the region λ 2894 Å to λ 2700 Å, but otherwise the lines employed in this investigation retard growth.

Generally the effect either of stimulation or retardation is greater when the control is one of rapid growth rate, but the reverse is the case at the red end of the visible spectrum.

Introduction

Recently many notable discoveries have been made dealing with the effect of radiant energy on protoplasm. Evidence has been adduced to show that evolution has received direct contribution from the influence of ultra-violet light and X-rays. Muller (1928) has observed mutations in the fruit fly (*Drosophila*) as a result of exposure to X-rays; new forms have suddenly appeared when parents have been subjected to this form of radiant energy, and these changes have been inherited by later generations. Goodspeed and Olsen (7) record similar suddenly appearing changes in the tobacco plant (*Nicotiana tabacum*). When flowering plants were exposed to X-rays in one experiment 70% of the seeds produced gave plants which differed markedly from the parents and also from one another. Hess (8) and others have demonstrated the value of irradiated ergosterol, which has been subjected to ultra-violet light, "one ounce of which will do the work of six tons of cod liver oil in preventing rickets". Higgins and Sheard (9) have demonstrated that the normal growth of the parathyroid gland which is essential for proper development is directly affected by exposure to sunlight, especially ultra-violet light. The experiments were performed on chicks, but the same principle no doubt applies to other forms. The investigation described in this paper shows that some frequencies or wave-lengths of radiant energy decidedly stimulate the growth of yeast while other wave-lengths inhibit its development. The harmful effects of ultra-violet light have been known for some time, the recognition of the beneficial properties is very recent. It is important to discover which wave-lengths are advantageous, and which disadvantageous, and under what conditions. Of the visible light the orange, yellow and green of the spectrum stimulate, while the blue and violet inhibit, and in the ultra-violet spectrum the near ultra-violet generally stimulates while the far ultra-violet inhibits the growth of yeast.

¹ Manuscript received March 20, 1930.

Contribution from the laboratories of the University of British Columbia, Vancouver, Canada, with financial assistance from the National Research Council of Canada.

² Professor of Botany, University of British Columbia.

³ Research Assistant.

Review of Recent Investigations on the Physiological Effect of Light on Plant Growth

The periods of growth and the growth curves in yeast have been studied by Priestley and Pearsall (17). If yeast cells from a culture that has ceased to grow are transferred to a fresh supply of nutrient medium, a "lag" period ensues when there is no growth, or little, this being followed by growth at normal rates. If a few yeast cells are sown into a definite quantity of suitable medium and allowed to grow until growth finally comes to a standstill, a growth curve is obtained which can be divided into distinct regions: (a), (b) and (c). In the region (a) growth of the mass is an exponential function of time, in region (b) the rate is directly proportional to time, and in region (c) there is a rapid decrease in rate of growth.

The effect of light upon the rate of growth may have one or several factors as its basis. Pincussen (13) describes the effect upon enzymes. A mercury vapor lamp was used, and solutions of diastase starch, etc., were prepared in a quartz flask. A non-irradiated diastase solution produced considerably more maltose from a starch solution than an equal amount of irradiated solution. A mixture of equal parts of the irradiated and the non-irradiated solutions gave more maltose than the arithmetic mean. The greater the proportion of non-irradiated diastase in the mixture, the greater the activity of the enzyme. Practically the same results are obtained when the starch and diastase are irradiated together as when treated separately.

DeJust (4) concludes from his experiments on the effect of ultra-violet light on sugars that there is little change in their reducing power and presumably in their physiological properties. However, Woodrow, Bailey and Fulmer (24) have adduced evidence of important sugar effects on yeast media. "By irradiating separately distilled water, a solution of the salts and the sugar solution, it was evident that the toxicity was entirely due to the effect of ultra-violet rays upon the sugar (sucrose). Similar toxicity was developed by irradiation of solutions of dextrose, calcium gluconate or glycerol. Upon exposure to ultra-violet light the yeast media developed a toxicity which increased with the length of time of the irradiation." It is concluded that the effect of ultra-violet light upon yeast in these media must be due in part at least to alteration in the composition of the medium, and not entirely to direct effect upon the organism. In these experiments the toxic factor results from the action of the short rays upon the sugar in the medium; for the study of direct action upon the cell, media must be selected which are not effected by the ray treatment.

Priestley (18) has performed some very interesting experiments on the growth of seedlings which show that very brief exposures of seedlings to light have very marked effects. A light exposure of one to two minutes per day to a relatively weak artificial light will remove effectively the most characteristic morphological features of etiolation, whilst the expanded leaf will fail to produce any signs of chlorophyll. This seems to dispose of the conclusion that photo-synthetic products of this period are concerned in morphological changes. If a

plant is exposed to light for a brief period during which growth is suspended by low temperature or the action of anaesthetics, the morphological changes mentioned still result when growth is allowed to resume in darkness owing to the previous light exposure.

The investigations of Higgins and Sheard (9) on the effect of light on the growth of seedlings give results remarkably in accord with the effect on the growth of yeast as described in this paper. Cucumber seeds were placed on moist blotting paper in the bottom of flower pots covered with (a) "Corning glass" with a transmitting range of λ 3900 Å- λ 3200 Å, (b) window glass transmitting to λ 3200 Å and (c) "Vita-glass" transmitting light to λ 2700 Å. The lesser wave-lengths used are stimulative and accelerate the rate, decreasing the time of germination, while the greater wave-lengths are inhibitive. Germination and growth are accelerated by irradiation in the near ultra-violet regions, λ 4000-3000 Å; wave-lengths below λ 2900 Å are definitely lethal.

From other experiments the same authors (21) have concluded that support is lent to the hypothesis that near ultra-violet irradiation aids in the growth of a cell or in the normal function of an organism which is kept in an unphysiological environment.

Priestley (18) describes the effect of light on osmosis. If sections cut from the plumar hook of a young plant grown in complete darkness are put in a 17% cane sugar solution, no sign of plasmolysis will be seen except in the pith; if, however, the plant is exposed to the electric light for two minutes each day for three successive days, the majority of the cells of the cortex will plasmolyze freely.

It has been shown by Rivera (19) that initial injuries caused by X-rays are often followed by the stimulation of growth. It is clear that green plants are not killed even by very strong dosage of X-rays, because following the initial arrest in development of the irradiated bud, there is almost always a development of a great number of buds of restitution. The root also derives advantage from the primary injury of the aërial portion, and often shows an extraordinary elongation under these conditions.

Ancel (2) exposed plants to ultra-violet light to discover the comparative harmful effect upon various regions of the plant. She states that in lentils and beans the rootlets suffered most, the main root less, and the stem least. It seems probable that chlorophyll has a protective capacity.

Garner, Bacon and Allard (5a) show that the daily time period of illumination is an important factor in the comparative development of vegetative structures and the storage organs such as seeds. Pfeiffer (14) finds that there are specific photo-periodic characteristics of plants; the optimum for the tomato is 12 hr., and for the buckwheat 17 hr.; the latter period is distinctly harmful for the tomato. Continuous light results in thinner leaves with palisades shorter or lacking.

Notable results have been obtained in plants by Goodspeed and Olsen (7). Tobacco (*Nicotiana tabacum*) in full flower was exposed to X-rays. Plants grown from seeds irradiated at this early stage included numerous variants, and

in one population of 200 plants 70% or more were variant individuals. A cytological investigation showed that chromosome disturbances had occurred, and that these modifications were in all probability primary to the external variations in form.

Elizabeth Kommerall (11) states that the effect on the germination of *Nicotiana tabacum* is proportional to the wave-length, if the light actually passing through the coat and reaching the seed contents is considered. Maximum absorption of light by seed coats she finds in the region of λ 5100 Å.

According to Shirley (22) the curve, showing the increase in dry weight and increase in light intensities, is a straight line in the winter, while in the summer it falls off at higher intensities. The same author also found that the plants studied produced more dry matter per unit light intensity under the complete solar spectrum than under any portion of it. Plants grow more effectively in the absence of the red, (λ 3700 Å- λ 5850 Å) than without the blue, (λ 5290 Å- λ 7200 Å) light.

In both the various strains of *Glomerella cingulata* and *Coniothyrium*, F. L. Stevens (23) shows that irradiation almost instantly initiates the development of reproductive structures in great numbers where they would not have occurred without irradiation; in no case, however, were structures initiated that were not known to be produced occasionally by these fungi in the natural course of events. The *Coniothyrium* normally produced but few pycnidia, these appearing after long continued growth; on radiation they were produced at once and in quantity. Certain races of *G. cingulata* that normally produced but few perithecia, and these in old colonies, produced them in great quantities at once, on irradiation. Other races of *G. cingulata* that have not normally been seen to produce perithecia did not yield perithecia on irradiation, but even these gave a greatly increased yield of acervuli.

Norma E. Pfeiffer, (14) grew certain plants in glass houses transmitting various wave-lengths of light, and recorded movements of stem leaf and root. In all cases she found that red light, blue light and shade inhibited growth to a greater extent than either the full spectrum minus violet, the visible range or the full spectrum.

Popp (15) removed definite regions of the spectrum in the blue-violet and noted the effect on plants. Eliminating all below λ 5290 Å resulted, aside from abundance of chlorophyll, in the plants having an etiolated appearance. Eliminating all below λ 4720 Å, produced the same effect, but to a lesser degree. Plants grown after elimination of all the ultra-violet displayed very little difference with plants grown in daylight. From these results it may be inferred that the ultra-violet rays are not indispensable, but the blue-violet end of the spectrum is necessary for normal vigorous growth.

According to J. D. Sayre (20) wave-lengths greater than λ 6800 Å are ineffective in the formation of chlorophyll in the seedling, but all other regions to λ 3000 Å are effective, provided the energy value is sufficient. For equal energy values in these regions the red rays are more effective than the green and the green more than the blue. The effectiveness increases to λ 6800 Å and then ceases abruptly.

As reported by Garner and Allard (5) the length of the day was found to have a marked effect on the flowering and fruiting of several plants; Arthur and Guthrie (3) on the other hand found that some plants respond much more readily than others to changes in the period of daily illumination.

Abbott (1) found that the rate at which *Formica dakotensis specularis* moved their pupae was directly proportional to the stimulating efficiency of the light for a given intensity. The yellow was found to be most effective, the white less and the red least effective; at low intensities no responses were obtained. All results produced curves which approached a constant value as intensities increased.

Experimental Work

Apparatus

The source of light used was a Cooper-Hewitt "Lab-Arc". It was operated on an alternating current of 110 volts, with a resistance of 12 ohms in series, and functioned under these conditions as a low pressure mercury arc. Generally 24-hour exposures were made, the intensity of illumination was low since a very narrow range of wave-lengths was used at any one time; in most instances the light used was composed of a single mercury line, and the irradiation was continuous. In view of the experiments of other workers interesting results might be obtained by intermittent exposures. The intensity of illumination in the case of each line produced with the instrument is being determined and will be recorded at a later time.

A monochromatic illuminator of Adam Hilger, Limited, fitted with quartz prism and lenses and reading directly to wave-lengths, was used to resolve the light. The instrument was standardized by readings on the sodium D-line. The yeast was placed in specially prepared quartz cells which fitted into a slot in front of the eye-piece of the monochromatic illuminator.

Media and Methods

The solid medium used for the maintenance of the stock culture was malt extract agar, made according to the following formula:

Malt extract.....	50 gm.
Agar.....	15 gm.
Water.....	1000 gm.

The malt extract was in the form of a desiccated powder put up by the Digestive Ferment Co., Detroit, Michigan.

Fleishman's yeast was the original source of the strain used for these experiments. A small quantity of the yeast was mixed with sterile water in a sterilized flask. The suspension was diluted until the individual cells were well apart, and then droplets were picked up with a sterile capillary tube and sown about an inch apart on the surface of agar plates. Colonies appeared in two days, and isolations were made from the colonies to agar slants. The slants were examined after a good growth had appeared; two distinct strains were noted, the first with large, oval to rounded cells, and the second with

small, oval to elongated-oval cells. The large strain was selected for the experimental work as it tended less to clumping and to filamentous formation, and thus simplified the counting of individual cells. This strain (which probably arose from a single cell), was transferred monthly to fresh agar slants, and was used throughout the year for the experimental work.

The liquid medium in which the yeast was cultured while under exposure to the monochromatic light was Cohn's solution. It was made according to the regulation formula, except that monobasic instead of dibasic calcium phosphate was used.

About 30 cc. of Cohn's solution was poured into an 150 cc. erlenmeyer flask which had been sterilized and was kept plugged with cotton wool. To this was added enough yeast on the end of a sterilized platinum needle to make the liquid slightly cloudy. The suspension was thoroughly shaken, and was then

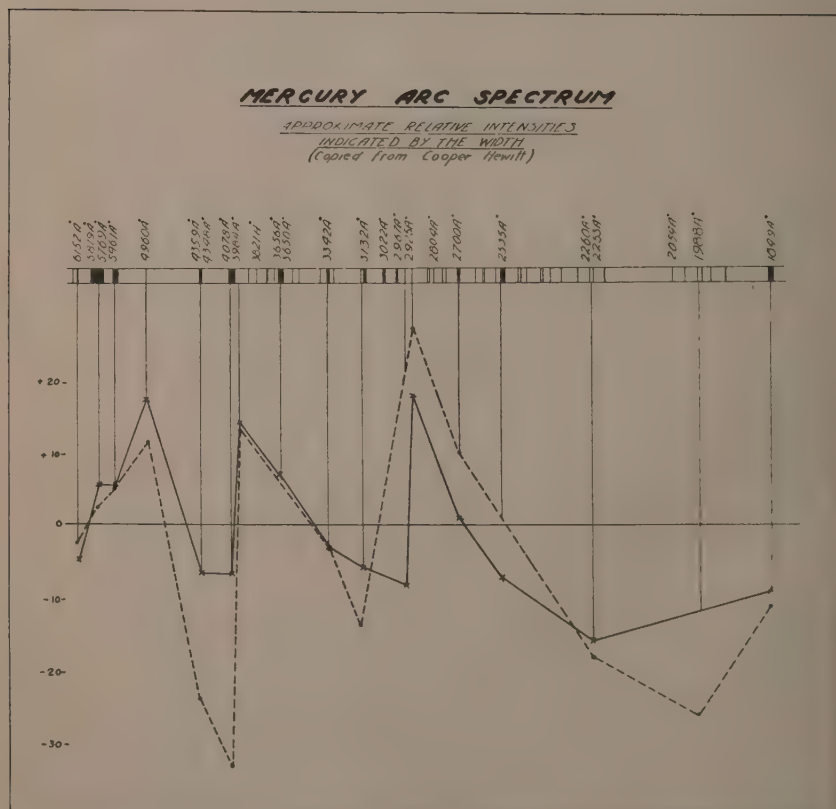


FIG. 1a. Specific effect of the energy of various wave-lengths (stimulation at the end of a 23-hour period is plotted as a positive ordinate, retardation as negative.) The effect on the irradiated cultures is shown by the full line, that on a control culture by the dotted line.

transferred with a sterilized dropper to each of the sterilized fused quartz containers used for exposure to the ray, to darkness and to room light, respectively. The containers were filled about three-quarters of the distance to the top, and plugged with sterilized cotton.

The liquid and solid media were sterilized in the autoclave at 15 lb. pressure for 20 min. The glassware and the fused quartz containers were sterilized daily in the dry oven at 150° C. for two hours or more.

The suspension to be exposed was placed in the slit of the monochromatic illuminator, while the two checks, one in room light, and one in the darkness of a cardboard box, were placed on a retort stand by the side of the monochromatic illuminator shaded from the light of the Lab-arc.

The counts were made with the aid of a Levy haemocytometer with Neubauer rulings. The suspensions were always agitated with the dropper or with a sterilized platinum needle before a sample was taken, as the yeast cells tend to sink to the bottom. Two separate samples were taken from each quartz container, with sterilized droppers, the droppers being rinsed between samples with sterilized water. From each sample 10 squares were counted, making a total of 20 counts from each quartz container. Seven squares in a diagonal from left to right of the upper ruling, and three squares in a diagonal from right to left of the lower ruling, were counted for each sample. The same squares were always used, so that the average would be as representative and consistent as possible.

The fresh culture prepared each day in the way already described, was exposed from 10 a.m. one day until 9 a.m. the following day, a period of 23 hours. At first, counts were made at 11 a.m., 1 p.m., 5 p.m. and at 9 a.m. The yeast, however, only began to bud between two and three o'clock, consequently the counts after the initial one were of little interest for this investigation until after five o'clock. After February 20th, the 1 p.m. and 3 p.m. readings were discontinued.

Results of Experiments

The records of the experiments have been tabulated (Table I), and have been illustrated by means of graphs. They may be described by reference to the same.

The effect of irradiation is modified by the primary growth condition of the yeast used in the experiment. As described by Priestly (17) there are four stages in the growth of a yeast culture (a) a primary lag, (b) a period of rapid growth during which the rate approaches a geometrical series, (c) a period of slower growth during which the rate is expressed as an arithmetical series, (d) a secondary lag which may continue for some time provided more favorable growth conditions are not restored. It is evident that it is very difficult to maintain constant experimental cultures, and it is to be expected that the various physiological conditions indicated by the growth rates may influence the effect of irradiation. In the experiments described below three kinds of control cultures have been distinguished, namely, (a) those of slow growth in which 10 cells per unit volume increase to 45 cells or less during a 23-hour

TABLE I
EXPERIMENTAL RESULTS

Experiment	Wave-lengths of radiation used	Growth phases of control	Yeast cells per unit volume after 7 hours			Yeast cells per unit volume after 23 hours			Effect of irradiation on number of cells after 23 hours		
			Irradiated cultures	Control cultures	Effect of irradiation on number of cells	Irradiated cultures	Control cultures	Effect of irradiation on number of cells	With control culture of ave. growth rate	With control culture of rapid growth rate	With control culture of slow growth rate
1	λ 6152-										
2	λ 6000 Å	Ave.	13.7	14.2	-0.5	51	58	-7.0			
3		Ave.	10.8	16.3	-5.5	65	68	-3.0	-5.0	(-3)	
		Slow	16.3	10.5	5.8	51	39	12.0			12.0
4	λ 5891-										
5	λ 5169 Å	Ave.	16.7	13.2	3.5	60	58	2.0		(2.0)	
6		Ave.	16.7	16.9	-0.2	62	53	9.0	5.0		
		Slow	14.2	9.0	5.2	54	36	18.0			18.0
7	λ 5461 Å										
8		Ave.	11.6	10.5	1.1	74	70	4.0		(4)	
9		Ave.	15.5	13.2	2.2	63	63	0.0	5.0		
		Ave.	13.1	14.2	-1.1	59	48	11.0			(11)
10	λ 4960-										
11	λ 4916 Å	Ave.	17.5	16.3	1.2	99	67	32.0			
12		Ave.	15.7	18.0	-2.3	75	69	6.0	17.0	(11)	
13		Ave.	23.0	15.6	7.4	86	70	16.0			(13)
		Ave.	17.1	12.5	4.6	58	45	13.0			
14	λ 4359-										
15	λ 4348 Å	Ave.	15.0	16.0	-1.0	63	64	-1.0			
16		Ave.	10.5	15.5	-5.0	32	46	-14.0			
17		Ave.	13.1	17.1	-4.0	63	70	-7.0			
18		Ave.	11.6	17.5	-6.0	40	46	-6.0	-7.0		(-10)
19		Rapid				49	77	-28.0		-25.0	
		Rapid	14.1	16.1	-2.0	58	80	-22.0			
20	λ 4078-										
21	λ 3984 Å	Ave.	16.0	13.0	3.0	48	61	-13.0			
22		Ave.	12.6	13.0	-0.4	50	52	-2.0	-7.0		
23	λ 4078 Å	Rapid	12.1	21.0	-8.9	55	81	-26.0			
24		Rapid	12.5	15.5	-3.0	38	75	-37.0		-32.0	
25	λ 3984 Å	Ave.	22.2	17.1	5.1	68	52	16.0			
26		Ave.	13.3	15.0	-1.7	78	65	13.0	14.0	(13)	
27		Slow	11.6	11.0	0.6	47	44	3.0			
		Slow	10.6	14.9	-4.3	51	44	7.0			5.0
28	λ 3663-										
29	λ 3650 Å	Ave.	14.1	12.9	1.2	56	53	3.0			
30		Ave.	12.7	13.7	-1.0	65	59	6.0			
31		Ave.				65	54	11.0	7.0		
		Rapid	16.3	13.5	2.8	64	74	-10.0		-10.0	
32	λ 3343 Å										
33		Ave.	17.1	18.2	-1.1	60	62	-2.0			
34		Ave.	13.5	12.2	1.3	65	69	-4.0	-3.0		
		Rapid	13.0	14.2	-1.2	78	78	0.0		-(2.0)	

TABLE I—*Continued*
EXPERIMENTAL RESULTS

Experiment	Wave-lengths of radiation used	Growth phases of control	Yeast cells per unit volume after 7 hours			Yeast cells per unit volume after 23 hours			Effect of irradiation on number of cells after 23 hours		
			Irradiated cultures	Control cultures	Effect of irradiation on number of cells	Irradiated cultures	Control cultures	Effect of irradiation on number of cells	With control culture of ave. growth rate	With control culture of rapid growth rate	With control culture of slow growth rate
35	λ 3145– λ 3132 Å	Ave.	13.0	12.0	1.0	60	66	–6.0	–6.0		
36		Rapid	11.2	12.5	–1.3	70	84	–14.0			
37		Rapid				83	85	–2.0			
38		Rapid	16.8	19.0	–2.2	58	84	–26.0		–14.0	
39	λ 2925 Å	Ave.	11.0	15.8	–4.8	55	65	–10.0			
40		Ave.	15.1	14.2	0.9	50	56	–6.0			
41		Ave.	11.0	11.5	–0.5	55	58	–3.0	–6.0		
42	λ 2894 Å	Ave.	14.0	19.2	–5.2	98	65	33.0			
43		Ave.				81	74	7.0	20.0		
44		Rapid	14.0	12.3	1.7	112	85	27.0		27.0	
45	λ 2700 Å	Ave.	12.6	12.9	–0.3	59	58	1.0	1.0		
46		Rapid	18.1	21.0	–2.9	90	80	10.0		10.0	
47	λ 2535 Å	Ave.	11.0	16.0	–5.0	50	64	–14.0	–7.0		
48		Ave.	22.0	26.0	–4.0	66	66	0.0			
49	λ 2253 Å	Ave.	11.5	15.5	–4.0	50	69	–19.0			
50		Ave.				46	58	–12.0	–16.0		
51		Rapid	12.0	15.5	–3.5	60	76	–16.0			
52		Rapid	11.9	18.0	–6.1	57	78	–21.0		–18.0	
53	λ 1988 Å	Rapid	18.3	18.5	–0.2	53	78	–25.0			
54		Rapid	12.0	13.1	–1.1	59	86	–27.0		–26.0	
55	λ 1849 Å	Ave.	9.5	11.0	–1.5	48	60	–12.0			
56		Ave.	17.0	13.0	4.0	35	50	–15.0			
57		Ave.	12.0	18.0	–6.0	53	63	–10.0	–12.0		
58		Rapid	15.5	13.8	1.7	66	71	–5.0			
59		Rapid	12.3	16.0	–3.7	70	86	–16.0		–11.0	

period; (b) those of average growth in which 10 cells increase to 45-70 cells; (c) those in which 10 cells increase to more than 70 cells during a like period. With one exception cultures of average growth have been irradiated by each of the mercury lines used in the experiment, and the results may be regarded as comparable the one with the other; cultures of rapid growth were irradiated with the greater proportion of the mercury lines, while cultures of slow growth

were used in a few instances only. It is recognized that the sub-divisions of control cultures used in these experiments are not entirely satisfactory since an average growth rate during the day period may result from the number of divisions in a culture which has recently passed the primary lag period, or in one which is approaching the secondary lag period. Occasionally in the description below, attention is drawn to such features in the culture but ordinarily these phases have not been specifically noted.

Range between λ 6152 Å- λ 6000 Å

The irradiation in this case is of low intensity and as obtained through the monochromatic illuminator is composed of two mercury lines, one toward the orange end of the red, and the other at the red-orange transition. The effect on the rate of cell division is somewhat varied. In the yeast growing at the average rate the result is slightly inhibitory (Fig. 1, 2, Exp. 1 and 2): the effect on the more rapidly growing culture is less inhibitory. In a slowly growing yeast, however, the result is a decided stimulation, (Fig. 3, Exp. 3). The stimulation of growth, when the control has a slow rate, holds for nearly all experiments with visible light.

Range between λ 5919 Å- λ 5769 Å

The range consists of two mercury lines of maximum intensity, in the yellow region of the visible spectrum. There is consistent stimulation of growth both at the end of the seven-hour period and of the 23-hour period. It will be noticed that the greatest stimulation is obtained in the more slowly growing culture (Fig. 4, Exp. 6), and decreases with the increasing growth rate of the control (Exp. 4, 5, Fig. 5 and 6).

λ 5461 Å

This is a single line in the yellow, near the yellow-green transition. A tendency towards stimulation is shown at the end of the seven-hour period followed by steadily increasing stimulation; again the greatest stimulation is produced when the control has the lowest growth rate. (Exp. 7-9. Fig. 7 and 8).

Range between λ 4960 Å- λ 4916 Å

Includes a green mercury line of rather low intensity. The initial effect is stimulation generally, which is continued throughout the 23 hours. One result shows retardation in the initial period followed by slight but steady stimulation. It is to be noted in this case that the control grows more rapidly than is usual, and this may account for the initial retardation. (Exp. 10-13, Fig. 9 and 10).

Range between λ 4359 Å- λ 4348 Å

A single line of intermediate intensity, at the violet end of the visible spectrum; it causes a steady and consistent inhibitory effect. It will be noted that in rapidly growing cultures the effect is of greater magnitude. (Exp. 14-19. Fig. 11 and 12.)

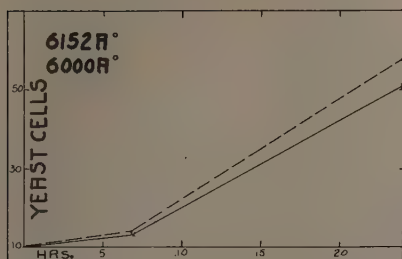


FIG. 1.

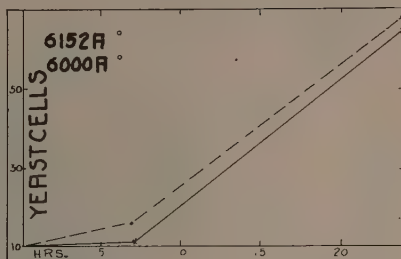


FIG. 2.

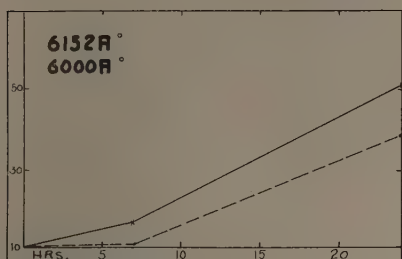


FIG. 3.

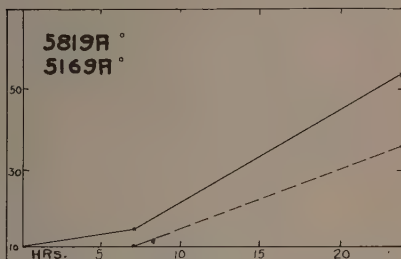


FIG. 4.

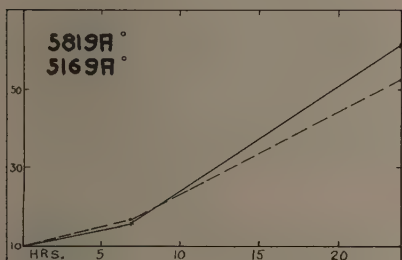


FIG. 5.

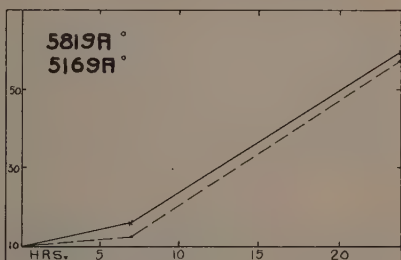


FIG. 6.

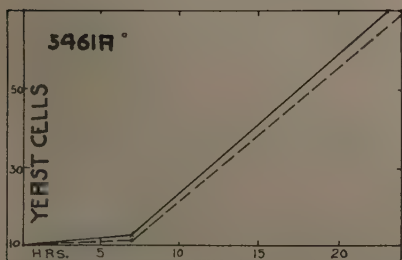


FIG. 7.

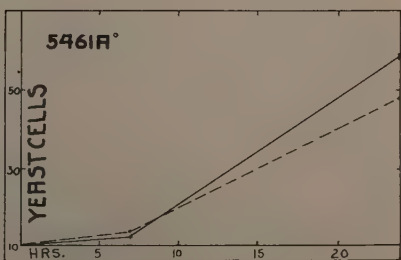


FIG. 8.

CONTROL CULTURE ——— IRRADIATED CULTURE ———

Specific effects of various monochromatic lines of the mercury arc upon the growth of yeast. The numbers of yeast cells are plotted against hours of irradiation.

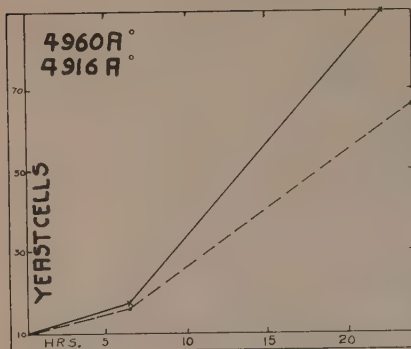


FIG. 9.

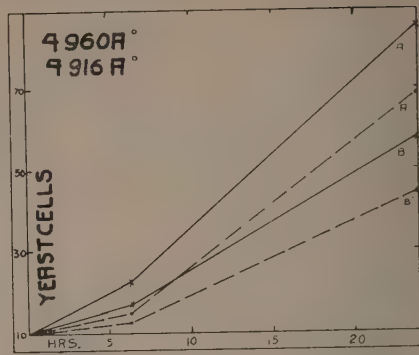


FIG. 10.

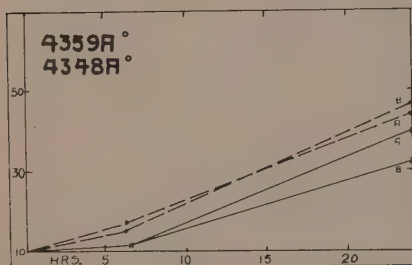


FIG. 11.

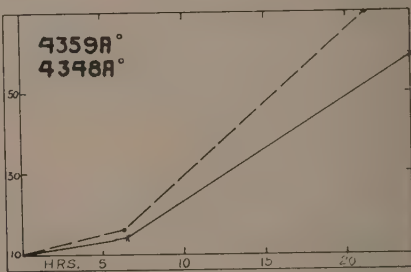


FIG. 12.

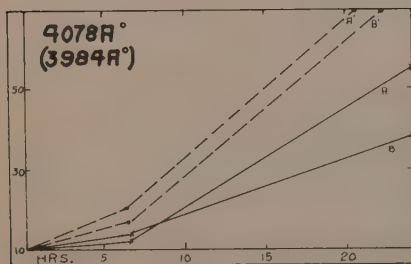


FIG. 13.

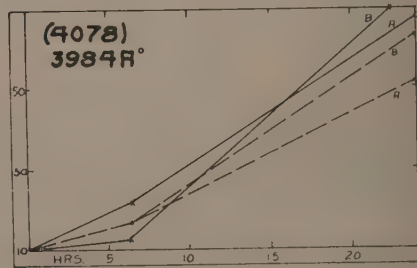


FIG. 14.

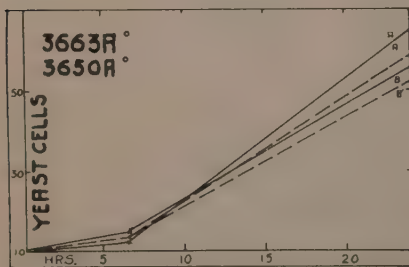


FIG. 15.

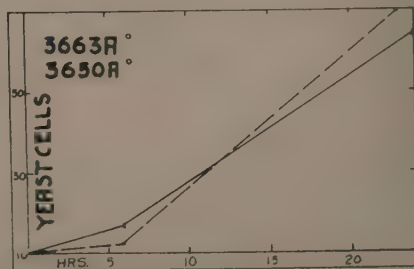


FIG. 16.

CONTROL CULTURE ---- IRRADIATED CULTURE —

Specific effects of various monochromatic lines of the mercury arc upon the growth of yeast. The numbers of yeast cells are plotted against hours of irradiation.

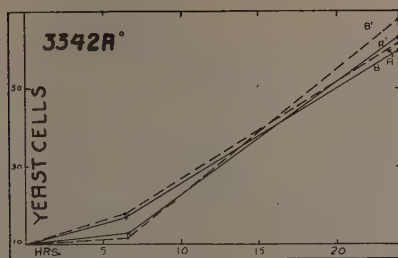


FIG. 17.

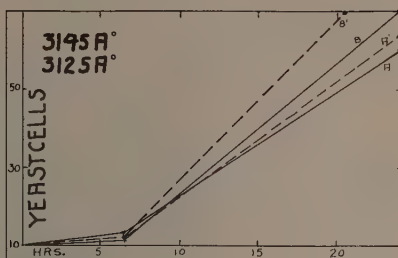


FIG. 18.

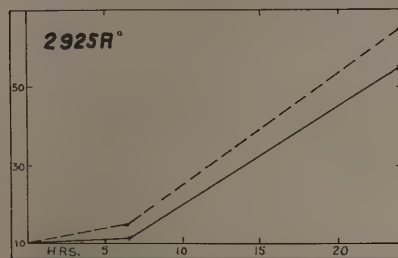


FIG. 19.

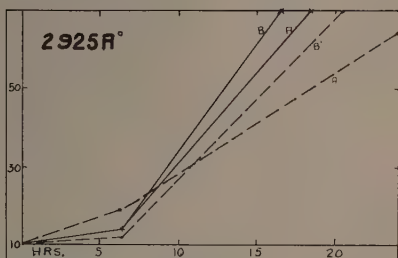


FIG. 20.

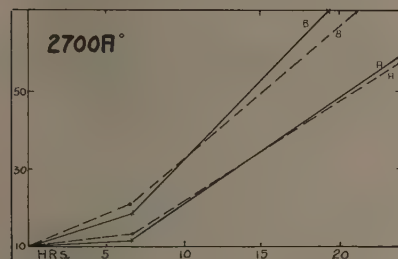


FIG. 21.

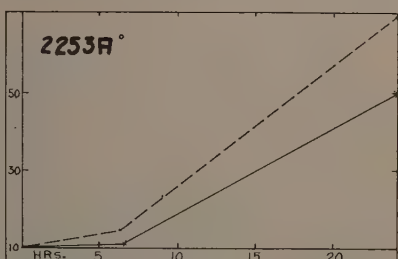


FIG. 22.

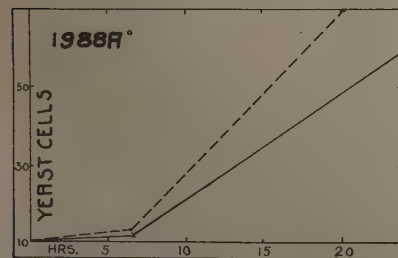


FIG. 23.

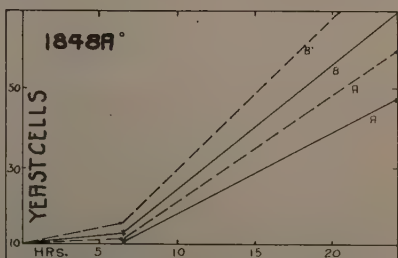


FIG. 24.

CONTROL CULTURE — — — IRRADIATED CULTURE —

Specific effects of various monochromatic lines of the mercury arc upon the growth of yeast. The numbers of yeast cells are plotted against hours of irradiation.

Range between λ 4078 Å- λ 3984 Å

Consists of two mercury lines of intermediate intensity, near the violet-ultra-violet transition. In this series of experiments both decided stimulation and decided retardation were obtained; moreover, the effect of stimulation or retardation during the first period was reversed in the second period, in nearly one-half of the experiments. The experiments may be interpreted by the presence of an inhibitory line (λ 4078 Å), the close proximity of a stimulative line (λ 3984 Å) in the mercury arc spectrum, and the probability that one predominates in some exposures while the second one does in others. It will also be noted that the two cases of greatest inhibition are those obtained upon rapidly growing cultures. (Exp. 20-27. Fig. 13 and 14.)

Range between λ 3663 Å- λ 3650 Å

Consists of a mercury line of somewhat more than intermediate intensity together with two or three lines of low intensity. Irradiation results in a slow but steady stimulation. In one case, however, there occurs a stimulation in a rapidly growing culture, and then a decided retardation.

 λ 3343 Å

A line of fairly great intensity, but having no very marked effect on the rate of growth of the yeast culture, there is a slight final retardation.

Range between λ 3145 Å- λ 3132 Å

A single mercury line of somewhat less than intermediate intensity. Slight retardation is noted at the seven-hour period, and continues throughout the period of irradiation.

Range between λ 2925 Å and λ 2894 Å

This region of the spectrum consists of at least three lines, λ 2925 Å, λ 3022 Å and λ 2894 Å, which may account for the inconclusive and contradictory results. In two cases there is decided stimulation, and in three cases a decided retardation. As in the previously described instance this region seems to present a rapid transition from energy causing a decrease in growth rate to that causing an increase.

 λ 2700 Å

A line of intermediate intensity causing an initial slight retardation followed by a gradual stimulation of the rate of division, a very consistent result.

 λ 2535 Å

A line of intermediate intensity of about the same magnitude as λ 2700 Å causes an initial retardation followed in one case by a slight stimulation, and in another by continued retardation; but in no case was the count of the control surpassed by that of the irradiated culture.

 λ 2253 Å

A line of very low intensity causing a consistent and fairly rapid retardation.

λ 1988 Å

A line of very low intensity having practically no initial effect but causing a very marked retardation after the seven-hour period.

 λ 1849 Å

A line of average intensity. The initial effect is slightly varied but the final effect after 23 hours is decided retardation.

Conclusions

It seems that there is no apparent relation between the specific intensity of the wave-lengths and their effects, and it is suggested that the frequencies of the various lines and their relation to the sizes of colloidal protoplasmic particles may be significant, that is, the phenomena may be associated with resonance.

Acknowledgment

The authors wish to acknowledge the helpful suggestions of Dr. G. M. Shrum of the Department of Physics, University of British Columbia, in matters pertaining to the sources and properties of light.

References

1. ABBOTT, C. E. *Ann. Entomol. Soc. Am.* 20, (1): 117-122. 1927.
2. ANCEL, SUSANNE. *Bull. soc. botan. France.* 73: 71-73. 1926.
3. ARTHUR, J. M. and GUTHRIE, J. D. *Mem. Hort. Soc. N.Y.* [3] 73-74: 2-3. 1927.
4. DEJUST, L. H. *Compt. rend. soc. biol.* 94: 328-330. 1926.
5. GARNER, W. W. and ALLARD, H. A. *J. Agr. Research* 18: 553-605. 1920.
- 5a. GARNER, W. W., BACON, C. W. and ALLARD, H. A. *J. Agr. Research* 27: 119-156. 1924.
6. GIBBS, R. D. *Trans. Roy. Soc. Can.* [5] 20: 419-426. 1926.
7. GOODSPEED, T. H. and OLSEN, A. R. *Am. J. Botan. Abs.* 15: vol. 10, 622. 1928.
8. HESS, A. E. *Science* 67, 1740. pp. 333-335. 1928.
9. HIGGINS, G. M. and SHEARD, C. *Plant Physiol* 11: (3): 325-353. 1927.
10. HOLM, A. E. *Science*, 67. 1738. pp. 424-425. 1928.
11. KOMERALL, ELIZABETH. *Jahrb. Wiss. Botan.* 66 (3): 461-512. 1927.
12. MARSHALL, H. T. *Am. Naturalist* 165-187. 1928.
13. PINCUSSEN, LUDWIG. *Seitscher*, 171, 1926.
14. PFEIFFER, NORMA. *Botan. Gaz.* 85: 427-436. 1928.
15. POPP, H. W. *Am. J. Botan.* 13: 716-737. 1926.
16. PRIESTLEY, J. H. and PEARSALL, W. H. *New Phytologist*, 25: (3) 145-170. 1928.
17. PRIESTLEY, J. H. and PEARSALL, W. H. *Ann. Botan.* 36: 142. 239-249. 1922.
18. PRIESTLEY, J. H. *New Phytologist*, 24: (5) 271-283. 1926.
19. RIVERA, VINCENSE. *Rio Biol.* 8: 505-539. 1926.
20. SAYRE, J. D. *Plant Phys.* 3 (1): 71-77. 1928.
21. SHEARD, C. and HIGGINS, G. M. *Plant Phys.* II (4): 461-473. 1927.
22. SHIRLEY, HARDY. *Am. J. Botan. Abs.* 15 (10): 621. 1928.
23. STEVENS, F. L. *Botan. Gaz.* 66 (2): 210-225. 1928.
24. WOODROW, J. W., BAILEY, A. C. and FULMER, E. T. *Plant Phys.* II (2): 171-175. 1927.

A RAPID METHOD FOR THE DETERMINATION OF ORGANIC NITROGEN IN LIQUIDS¹

BY REUBEN B. SANDIN² AND NORMAN M. STOVER³

Abstract

A method for the rapid determination of organic nitrogen in liquids is described. It depends upon the liberation of amino, amido, etc. nitrogen as ammonia by an alkali fusion of the organic material. The ammonia is absorbed in excess saturated boric acid solution, and then a titration with standard acid is carried out, using bromophenol blue as the indicator.

Introduction

Very recently the alkaline combustion method for the determination of organic nitrogen has been revived by Jaramillo (5). He suggests that, for the determination of nitrogen in liquids such as milk or beer, a measured volume of the liquid be evaporated to dryness in a shallow porcelain dish lined inside with tin foil free from holes, in order to facilitate the transfer of the residue to the combustion tube. The authors have found this procedure to be unnecessary. The length of time required for a determination is thereby materially shortened, and the danger of loss of nitrogen, which might result during evaporation, eliminated.

Nitrogen determinations have been carried out on samples of urine, milk and beer. The results obtained compare favorably with those obtained by the Kjeldahl method. The method described here should be of value, especially in the clinical laboratory, since the operation can be carried out in less than 30 min.

It should be mentioned here that Bergell (1) recommends using, instead of the time-consuming Kjeldahl method for obtaining total nitrogen in urine, the soda lime (fusing) method of Dumas. This is performed in quartz vessels, and can be done in 10 to 20 min. Evidently this method has been forgotten.

Experimental Part

The apparatus used consists of a copper tube 43 cm. long and 3.5 cm. in diameter, fitted with a rubber stopper carrying a Pyrex Kjeldahl connecting bulb C, and a small copper tube A bent as shown. The bulb C is filled with small pieces of Pyrex glass rodding. A tube D, also of Pyrex glass, acts as an air condenser. The latter may be replaced by a small water condenser, in which case it is not necessary to have the flask E immersed in cold water during the determination.

¹ Manuscript received February 25, 1930.

The work described in this paper is an outgrowth of a main attempt to find a simplified nitrogen determination.

² Associate Professor of Chemistry, University of Alberta.

³ Lecturer in Chemistry, University of Alberta.

Five cc. of urine or milk (20 cc. of beer) is introduced into B, and to it is added 10 gm. of sodium hydroxide, or better still a mixture of 5 gm. of sodium hydroxide and 5 gm. of potassium hydroxide, which is close to the eutectic mixture of melting point 185°C . 50 cc. of saturated boric acid* solution (7) and 100 cc. of water are placed in the flask E, which is kept in cold water, and tube B is made free from air by a rapid stream of natural gas** bubbling through a solution of sodium hydroxide. The lower end of B is heated for a

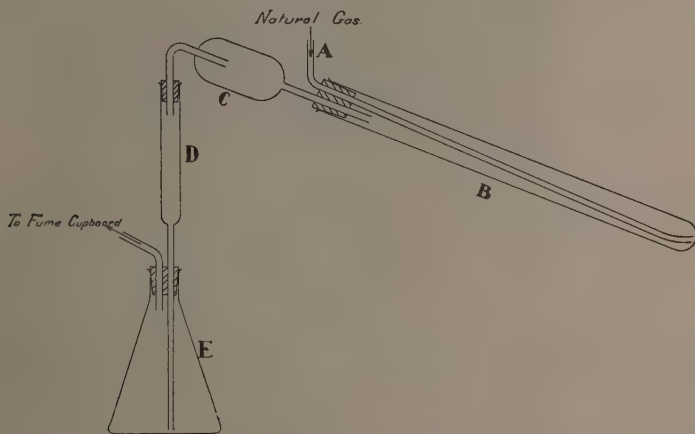


FIG. 1 The apparatus used in the determination of nitrogen

distance of about four inches to a dull red heat. About 15 min. is the required time of heating. During this time and for about five minutes after the heating is completed, natural gas is allowed to pass through the system. It is also necessary at the end of the experiment to heat C to dryness in order to drive over all the ammonia. Titration is then carried out with 0.1 N sulphuric acid, using bromophenol blue as the indicator. The end point of the titration is taken as the disappearance of the purple color (6).

Tube B is best cleaned out with a little commercial concentrated hydrochloric acid.

Some of the results obtained are shown in Table I.

*The boric acid was crystallized twice from water.

**The natural gas used contained approximately 93.5% methane, 3.5% ethane, 3% nitrogen and a trace of carbon dioxide. Coal gas or water gas should work as well, provided care is taken to remove oxygen, carbon dioxide and ammonia.

TABLE I
ANALYSES FOR NITROGEN

	Kjeldahl method, per cent	Alkaline combustion method, per cent
Urine 1	1.10	1.09
2	0.83	0.83
3	1.06	1.07
4	1.33	1.33
5	0.98	0.97
6	0.65	0.65
Milk 1	0.48	0.47
2	0.47	0.46
3	0.47	0.47
4	0.48	0.48
Beer 1	0.08	0.08
2	0.08	0.08
3	0.09	0.08

Discussion

The results of analyses as shown in Table I support the reliability of the method. As far as Jaramillo's work on the alkali fusion of dry materials is concerned, more work must be done in connection with it. The authors believe that the discrepancies shown in his analyses are not due to leaks, but to alkali mechanically carried over. Regarding the mechanism of the reaction involved, the authors believe that it is an oxidation reaction, with the fused alkalies as oxidizing agents, and a concomitant liberation of ammonia. Fry and his collaborators (2, 3, 4) have found that fused sodium and potassium hydroxides at temperatures between 450° and 500° C. cause complete oxidation of alcohols, sugars, cellulose, etc. to carbonates, methane and hydrogen.

It is hoped to extend this work and apply it especially to the determination of nitrogen in wheat.

References

1. BERGELL, P. Deut. Med. Wochschr., 38: 1980-1981. 1913.
2. FRY, H. S. and OTTO, EARL. J. Am. Chem. Soc., 50: 1122-1131. 1928.
3. FRY, H. S. and SCHULZE, E. L. J. Am. Chem. Soc., 50: 1131-1138. 1928.
4. FRY, H. S. and OTTO, EARL. J. Am. Chem. Soc., 50: 1138-1144. 1928.
5. JARAMILLO, G. J. Am. Chem. Soc., 48: 2453-2454. 1926.
6. SCALES, F. M. and HARRISON, A. P. J. Ind. Eng. Chem., 12: 350-352. 1920.
7. SPEARS, H. D. J. Assoc. Official Chem., 5: 105-108. 1921.

INVESTIGATION OF THE REACTION BETWEEN HYDROGEN CHLORIDE AND THE THREE BUTYLENES¹

BY C. C. COFFIN,² H. S. SUTHERLAND³ AND O. MAASS⁴

Abstract

The reactions between α , β and γ -butylenes and hydrogen chloride are investigated. It is shown that, of the butyl chlorides produced, only the secondary chloride is formed in the reactions with α - and β -compounds, and only the tertiary chloride in the reaction with the γ -compound. In the case of the first two reactions (with α - and β -compounds) it is shown that a secondary product (an octyl chloride) is formed. Its possible structure, 3-methyl-4-chloromethyl hexane for the reaction with the α -compound and 2-chlor-3, 4-dimethyl hexane for the reaction with the β -compound is indicated, and it is shown that these decompose into an octylene and hydrogen chloride. The mechanism of the various reactions and its relation to the rates of reaction is suggested.

Unsaturated hydrocarbons and the hydrogen halides do not always react with one another in the absence of catalysts. A series of investigations (3, 4, 5, 7) have been carried out which tend to show that the rate of reaction between the pure hydrocarbon and pure hydrogen halide depends on the degree of molecular attraction; thus ethylene and acetylene, which do not react with hydrogen halides, also show no tendency towards molecular compound formation, whereas the reverse is true of propylene and the butylenes which react readily in the liquid state.

A new view of the influence of temperature and pressure on the velocity of a reaction has been put forward (6) already. The idea that the various forms of thermal energy influence the rate of chemical reaction in various ways was advanced in 1918 and published in 1922. The kinetic energy of rotation and translation actually hinders chemical combination, since it hinders molecular complex formation, whereas vibrational energy furthers it. Thus the attraction of one molecule for another plays an important part in considering the velocity and products of the chemical reaction.

This paper deals with a side issue of the above investigation. Where a reaction takes place in one of the systems mentioned, it does so in two ways: the principal reaction, which is to be expected, and a secondary one, which is not a simple addition reaction. It is the nature and relative amounts of the products in the case of butylene reactions which is to be described in this paper.

A short review of the experiments carried out with propylene (7) will serve as an introduction. When equal molecular proportions of propylene and hydrogen halide, (hydrogen bromide or hydrogen chloride), are mixed, the hydrogen halide is not all used up when the reaction is complete. The excess is due to

¹Manuscript received March 12, 1930.

Contribution from the Physical Chemistry Laboratories, McGill University, Canada. This paper is based on a thesis presented by H. S. Sutherland to the Faculty of Graduate Studies, McGill University, in partial fulfilment of the requirements for the degree of M.Sc., 1929.

² Holder of a Fellowship under the National Research Council of Canada.

³ Holder of a Bursary under the National Research Council of Canada.

⁴ Professor of Physical Chemistry, McGill University.

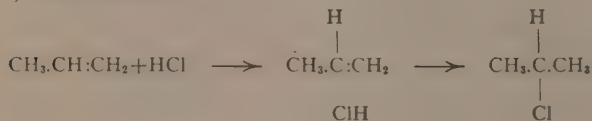
a secondary reaction involving two propylene molecules and one of hydrogen halide. The greater the velocity of the reaction, the smaller is the extent to which the secondary reaction takes place; this was shown by measuring the amount of hydrogen halide left over in a 1:1 mixture at various temperatures. For example, at -78.5°C . in the case of hydrogen bromide and propylene, 30% of hydrogen bromide is left over, whereas at 0° , where the reaction is much quicker, only 10% is left over when the reactions are completed. The secondary product in this case was identified as hexyl bromide.

A more complete study of the products of the propylene-hydrogen chloride reaction has been made (8). The substances were allowed to react in the liquid state at low temperatures, and the products were separated by low temperature fractionation. Three substances were isolated, isopropyl chloride, an "oil", and a slight amount of a very high boiling product designated as "tar". The isopropyl chloride was identified by its vapor pressure curve. Molecular weight determinations were in good agreement with the theoretical molecular weight for a hexyl chloride. Chlorine analyses confirmed this. The boiling point of the hexyl chloride appeared to lie between 110°C . and 111°C ., but, since decomposition was noticed at the higher temperatures, it was probably higher than this. This decomposition seemed to be reversible at lower temperatures. Due to the small quantities of the "tar" present, rough determinations only could be made on this fraction. It appeared to be a hydrocarbon of molecular weight 260, boiling at 163°C .

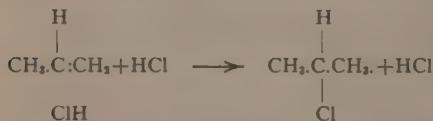
With regard to the formation of the hexyl chloride, it was considered that two molecules of propylene condensed with one of hydrogen chloride.

Several suggestions as to the possible course of the propylene-hydrogen halide reaction were made:

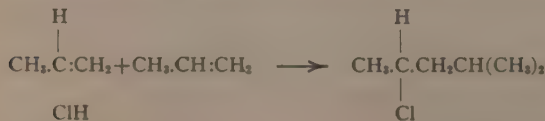
(a) Monomolecular:



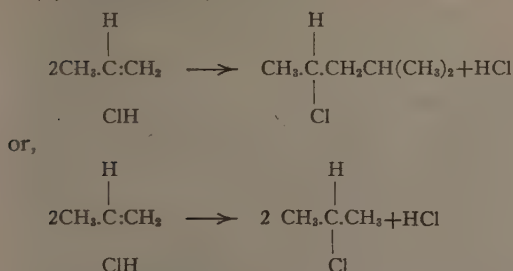
(b) Monomolecular compound catalyzed by hydrogen chloride:



(c) Bimolecular, between propylene and the molecular compound:



(d) Bimolecular, between two molecular compounds:



Reactions (a) and (c) were rejected on the grounds that there is a diminution in the rate of reaction as the concentration of propylene is increased. The objection to (b) was that the ratio of the products formed was quite independent of concentration above about 2:1, while at higher concentrations, should reaction (b) hold, *isopropyl* chloride should be formed almost exclusively.

Reaction (d) is considered as a likely explanation, since it accounts for the products obtained, and accounts for the fact that experimental conditions may alter the relative amounts of each product. Since it is bi-molecular, between the two molecular compounds, excess propylene would decrease the rate of reaction, which agrees with the experimental fact. However, it was not concluded that this reaction took place to the exclusion of all others, but that it represents the main course of the reaction.

In consideration of the various methods by which such a reaction could take place, four compounds are given as possible products: 2-chloro hexane, 1-chlor-2-methyl pentane, 2-chlor-4-methyl pentane, and 1-chlor-2, 3-dimethyl butane.

Examination of the literature showed that of the eight hexyl chlorides recorded, three decomposed on boiling, and one of these possessed a chlorine on the end of the chain. Thus it is probable that, of the four possibilities given, that possessing a chlorine atom on a secondary or tertiary carbon atom would be the correct compound. 2-chloro-4-methyl pentane (not recorded in the literature) is the only one of the four which does not have its chlorine on the end of the chain, and is thus considered to represent the formula for the hexyl chloride. The authors also suggest the possibility that it might be 1-methyl-1-chlor pentane.

More recently, work has been done in this laboratory on the velocity of the butylene-hydrogen halide reaction, and its relation to molecular attraction, which is published elsewhere.

Experimental

It was decided to carry out the reaction on as large a scale as possible in order to produce an appreciable amount of secondary products. The dimensions of the apparatus had to be carefully chosen, so that it would be suitable for the following operations. Large amounts of substances of high vapor pressure had to be sealed off in glass bulbs capable of standing 25 atmospheres, and these

had to be inserted in a distilling apparatus. Since the reaction mixture at the end contained a large amount of low boiling substances (uncombined reactants and primary product), and relatively small amounts of high boiling substances, (secondary products), the distilling apparatus had to be designed to overcome the difficulties in the fractionation of such a mixture.

In general the separation of products was carried out by low temperature vacuum distillation. The high-boiling secondary products could not be purified at low temperatures and hence had to be heated.

The main products of the reactions were identified by a melting point or boiling point. The lack of data and scarcity of the pure substances made the structural identification of the secondary products more difficult. By molecular weight determinations, chlorine analyses, bromine absorption and so on, they could be placed in a definite class. Their probable structure was then indicated.

Preparation and purification of the reagents

The hydrogen chloride was prepared in the usual way by the action of sulphuric acid on C. P. sodium chloride, covered with concentrated hydrochloric acid. The main impurity was water. The gas was passed through two sulphuric acid bubblers, two phosphorus pentoxide tubes, and condensed in a bulb by means of liquid air. It was then distilled through another phosphorus pentoxide tube into a second bulb, whence it could be distilled back and forth over the drying tube until all the water had been removed. The "heads" and the "tails" of all distillations were rejected. Usually after passing through the pentoxide tubes, three or four times, the gas was thoroughly dry.

The butylenes were made by the dehydration of the corresponding alcohols by passing them over alumina or phosphoric anhydride, at 360° C. (1, 2).

The alumina was prepared by the precipitation of aluminum hydroxide from aluminum nitrate. The hydroxide was washed thoroughly, moulded into small balls and dried at 110° C. In order to prepare the phosphoric anhydride tube, phosphorus pentoxide was allowed to distil through an electrically heated tube filled with pumice. The pumice became impregnated with the anhydride, thus giving a very large contact surface.

α - and β -butylene were produced by dehydrating normal butyl alcohol, the α -isomer predominating. The best yields of β -butylene were obtained when phosphoric anhydride was used as the dehydrator. These isomers were separated by low temperature fractional distillation. *Isobutylene* was obtained by dehydrating *isobutyl* alcohol over alumina at 360° C.; it was free from its isomers, and relatively easy to purify.

All of the butylenes were dried and purified in the same manner, by freezing out the water and by lower temperature fractionation. The wet butylene was condensed in bulb A (Fig. 1), and distilled into bulb B. The three-way stop-cock V was then opened and the liquid butylene allowed to rush into

bulb C (C having been previously evacuated). The water was left as ice on the side of B or caught by the glass wool at the base of the bulb. Since each bulb was kept at $-78.5^{\circ}\text{C}.$, the ice had practically no vapor pressure, and the butylene was dried effectively. An incidental experiment showed that the butylenes could be dried over anhydrous calcium chloride at $-10^{\circ}\text{C}.$, without danger of polymerization.

The dry butylenes were then distilled into the fractionating apparatus (Fig. 2). This consisted of a bulb A with a magnetic stirrer, connected with six receivers B_1 , B_2 , etc., a manometer C, and with a vacuum pump at D.

The apparatus was evacuated and the fractionation commenced by cooling one of the receivers to $-78^{\circ}\text{C}.$ and allowing the fractionating bulb to warm. The magnetic stirrer was kept in motion continually, since a good separation could not be obtained unless the surface of the liquid was kept broken. The

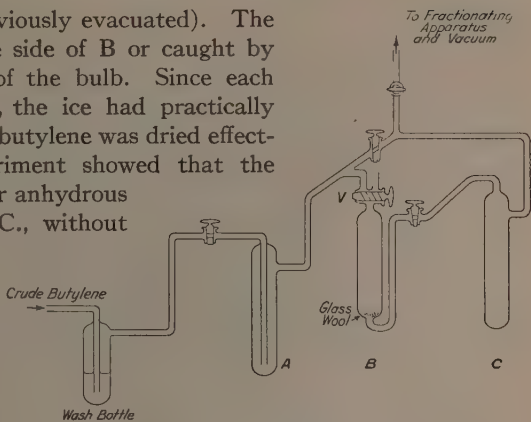


FIG. 1. Drying apparatus

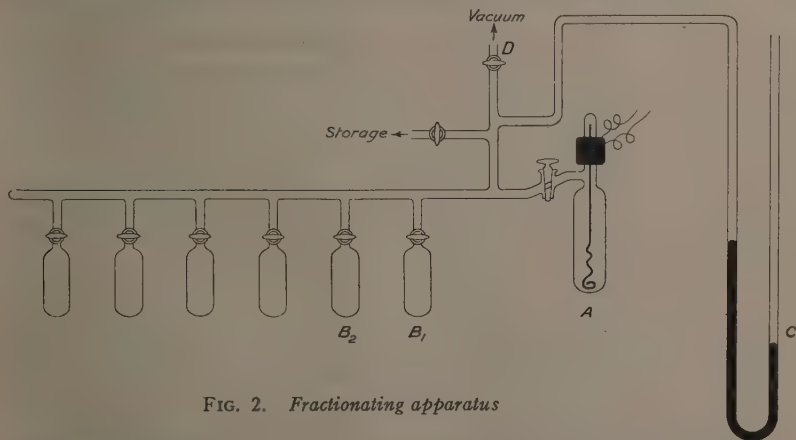


FIG. 2. Fractionating apparatus

liquid was divided into three parts, which in turn gave three fractions, and so on. Fractions of equal vapor pressure were united and refractionated, the large middle fractions of these portions only being stored as pure butylene. The boiling points of the isomers were found to be as follows:

α -Butylene, $-6.2^{\circ}\text{C}.$; β -butylene, $+1.1^{\circ}\text{C}.$; γ -butylene, -6.7° ; all three at 760 mm.

The purity of the α -isomer was assured by the fact that it would not freeze in liquid air.

Method of mixing

The apparatus used for mixing the reagents is shown in Fig. 3. A and B are storage bulbs for the reagents. M_1 is a manometer. C is a container of known volume kept in a constant temperature bath for measuring the amounts of reagent used. M_2 is a manometer connected separately with the container of constant volume. D is the reaction bulb.

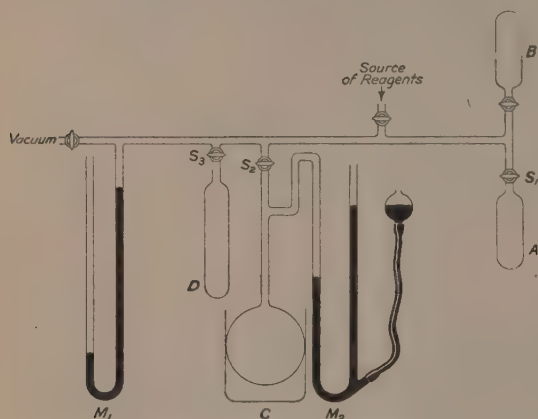


FIG. 3. *Mixing apparatus*

The apparatus was first evacuated, then flushed out with the reagent used, and evacuated again. The stopcock S_1 was opened and bulb A containing the condensed reagent allowed to warm by removal of the Dewar flask used in the condensation. As the bulb warmed up, the vapor expanded into C, through S_2 , but was prevented from entering into D by keeping S_3 closed. When the pressure became approximately

atmospheric, S_1 and S_2 were closed, and the pressure and temperature in C read accurately. The lines were then evacuated, and the gas condensed in D, by means of liquid air. The pressure and temperature of C were read after the condensation, and the relative amounts of reagents which were added each time calculated.

In the case of *isobutylene*, the hydrocarbon, and hydrogen chloride were added alternately, the flask of the distilling apparatus (A, Fig. 1) being used as the reaction bulb. The reason for this was that *isobutylene* and hydrogen chloride react almost instantaneously at -78.5°C ., and if large amounts were to react at one time, quite large pressures would be built up due to the heat of reaction. No such precautions were necessary in the case of the reactions with the α - and the β - compounds, since the reaction took place very slowly even at 0°C . Pressure, due to uncombined reactants, however, created a real difficulty in carrying out these latter reactions. The vapor pressure of a mixture of butylene and hydrogen chloride is of the order of 20 atmospheres, hence great care was necessary in the construction of the glass reaction bulbs. These bulbs were made of heavy glass, whose walls were 3 mm. thick and whose inside diameters were 21 mm. They held 3.45 cc. per cm. length and were about 25 cm. long. Each contained about 60 cc. of the condensed reagents.

The bulbs, sealed at liquid air temperatures, were placed in an iron protector and allowed to warm up in an ice bath. The first reaction bulb with the α -compound exploded after six hours, but the second attempt was successful.

The proportions of hydrocarbon to hydrogen chloride in the bulbs were as follows:

γ -Butylene to hydrogen chloride 1.00:0.999,

α -Butylene to hydrogen chloride 1.00:1.03,

β -Butylene to hydrogen chloride 1.00:1.006.

Methods of separation

Low temperature fractionation, in vacuo, was the general method employed for the separation of the products. It was found to be very easy to separate and purify the butyl chlorides (primary products), since they were produced in the largest amounts and had relatively low boiling points. The pure products were obtained after four or five fractionations, as was shown by vapor pressure determinations.

It was impossible to purify the high boiling fractions by this method, due to their low vapor pressure at room temperature. Hence it was necessary to remove them from the apparatus, to a smaller and more suitable one. The products were then fractionated in vacuo by gentle heating, but even at temperatures much below their boiling points, decomposition was noted. Since relatively large "middle fractions" had to be separated out, and several fractionations were necessary, the recovery of the individual secondary products was poor, usually of the order of one cubic centimeter.

Methods of analysis and identification

In the case of the main products, boiling points and freezing points were used as a means of identification. The boiling points were determined by placing some of the liquid to be identified in an open bulb with a standard thermometer suspended in its neck, and refluxing the liquid on the walls. Boiling points so obtained checked well with those given in the literature. A small amount of the liquid was sealed in a bulb and placed in a cold ether bath, in order to determine the freezing point. The bulb was shaken continually in order to prevent supercooling. The temperature of the bath was measured with a standard thermometer. The freezing points determined were quite sharp, showing the purity of the substances.

Analysis for the chlorine was carried out in the following way. A small piece of metallic sodium was dissolved in about 10 cc. of liquid ammonia. After the deep blue color had disappeared, showing that sodamide had been formed, a weighed sample of the unknown substance was added. The mixture was then allowed to warm up and the ammonia was evaporated. Water was added and the strongly alkaline solution was made acidic with nitric acid. The chloride ion was then determined by means of standard silver nitrate and potassium thiocyanate solutions. Due to the small amounts of pure secondary products obtainable a pycnometer of capacity 0.5 cc. was made, to facilitate weighing.

In determining whether or not a compound was unsaturated, the addition of bromine was tried. Although in this manner, unsaturation could be definitely established, yet it was impossible to make any quantitative determination due to the fact that in a short time bromine entered the chain by substitution.

An unsaturated compound decolorized 3 or 4 cc. of bromine water immediately, and the bromide formed separated out as an oil. A saturated compound held the bromine color for one minute or two after the first two drops, but then gradually lost it. However, it was useful to be able to determine whether a compound was unsaturated or not, for in the event of such a compound showing no chlorine it followed that an unsaturated hydrocarbon could be identified.

The cryoscopic method, with benzene as a solvent, was used for molecular weight determinations, and consistent results were obtained. The unknown substance could not be recovered quantitatively, so that it was used again for qualitative tests only (addition of bromine).

Results

In the following discussion, the "main product" designates the product of the main and simple reaction, including the formation of a butyl chloride. The "secondary products" refer to the products of any other reaction which may take place.

α -Butylene

The main product of the α -butylene-hydrogen chloride reaction was found to have a boiling point of 67.2° C. at 754 mm. pressure. This agrees well with the value given in the literature for secondary butyl chloride, (67.3° C. at 767 mm.) Since it was well known that a butyl chloride was produced, and since the boiling points of the other butyl chlorides differ by at least 10 degrees from this point, no other means of identification was necessary. The formation of this product follows the general rule that the chlorine adds on to the carbon atom attached to the smallest number of hydrogen atoms. No primary butyl chloride was found. The absence of this product was shown by the sharpness of fractionation between the high boiling secondary product and the main product.

The secondary products decomposed as soon as they were warmed in vacuum. A small amount which had not been heated was shown to be unsaturated by the immediate addition of bromine. In view of the fact that butylene and hydrogen chloride were the only reactants, it is rather inconceivable that any unsaturated product could be a chloride. The decomposition products of this secondary fraction were hydrogen chloride and a colorless liquid which had a relatively high boiling point. This liquid was proved definitely to be unsaturated. Its molecular weight was determined and found to be 113. The molecular weight for an octylene is 112. This points to the fact that at least part of the secondary product decomposed into hydrogen chloride and an octylene. The simplest compound which could do this would be an octyl chloride, although a chloride containing 16 carbon atoms could do the same. Since unsaturation was noted before heating, it was decided that the secondary product, in this reaction, was a mixture of octylene and an octyl chloride, which

decomposed further on heating. A trace of semi-solid residue was noted after the decomposition of the secondary products, but it was too small to be removed from the bulb.

β -Butylene

In the case of the β -butylene reactions, secondary butyl chloride was again produced. In this case it is the only butyl chloride which is theoretically possible. Its boiling point was 67.3° C. at 761.4 mm. pressure, agreeing perfectly with the value found in the case of the reaction with α -butylene.

More of the secondary products were produced in this case than in the former (α -butylene), as was expected from the velocity curves. Since decomposition was again possible, some of the crude products were set aside for qualitative tests. Although on distillation there was a slight decomposition, as noted by three or four bubbles of hydrogen chloride produced, yet it was not comparable to the decomposition of the secondary α -butylene products. Qualitative tests on the crude products showed unsaturation. This was confirmed by a relatively large (about 1 cc.) low boiling fraction, which showed unsaturation very distinctly. A molecular weight determination gave an average value of 105.3 (103, 107, 106). Chlorine content, 0.9%. Since there could be no carbon, hydrogen and chlorine compound of that molecular weight showing less than 33% chlorine, it was evident that a slight amount of primary product was present, and that the secondary product was an octylene (molecular weight 112).

A higher boiling fraction was separated, whose molecular weight was 145 (142, 143, 150). This compound was quite saturated; the coloration caused by two drops of bromine water remained for over five minutes. Chlorine content, 20.4%. An octyl chloride has a molecular weight of 148.5 and a chlorine content of 23.5%. Thus there seems to be little doubt, that there is an octyl chloride produced. The small discrepancies in the results are in the direction of the slight decomposition, which was observed. There was no residue left after distillation of the octyl chloride.

γ -Butylene

As was expected, in this case there was no secondary reaction. A minute trace of a semi-solid residue was left after the low temperature distillations, but was too small for identification.

The main product proved to be tertiary butyl chloride; it melted at -26.5° C., 0.5 degree higher than recorded in the literature. The melting points of the other chlorides are more than 100 degrees lower. It was shown to be a pure product by the fact that the melting points of different fractions were taken, and they were all the same.

A small amount of extremely low boiling fraction was also separated. Its boiling point was slightly below zero, and bromine water absorption confirmed the suspicion that it was a very small amount of uncombined butylene. This point rather confirms the fact that no secondary reaction takes place, because

an excess hydrogen chloride would be present should such a reaction occur. The reaction mixture at the start contained a slight excess of butylene on the basis of a 1:1 ratio, and this was evidently recovered.

Summary of results

A summary of the results, together with the time the reagents were allowed to react, and the percentage reaction based on excess hydrogen chloride left (according to velocity curves) is given below. The percentage reaction agrees very well with the amount of primary product formed.

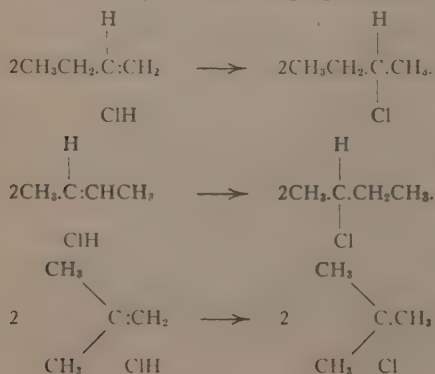
TABLE I
EXPERIMENTAL RESULTS

Reagents	Primary products	Secondary products	Time	Percent reaction
Butylene + HCl.	Sec. butyl chloride (only)	Octylene, Octyl chloride (Tar?)	20 days 0° C.	74
Butylene + HCl.	Sec. butyl chloride	Octylene, Octyl chloride, (Tar?)	35 days 0° C.	62
Butylene + HCl	Tertiary butyl chloride (only)	None	Instantaneous -78.5° C.	

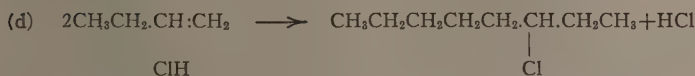
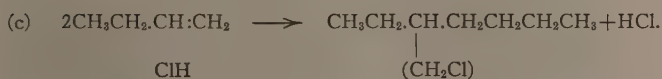
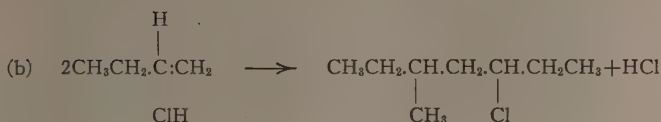
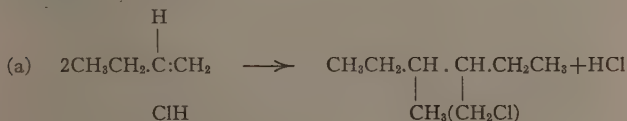
The relative amount of secondary products in all three cases is inversely proportional to the velocity of the reaction.

Conclusion

It has been shown that in the propylene reaction corresponding to the butylene reactions, two loose molecular compounds reacted, and either split off hydrogen chloride to form the secondary product, or underwent a re-arrangement to form the primary product. Considering the formation of the primary product in the present research, an analogy to the propylene reaction may be drawn, as shown by the following equations:

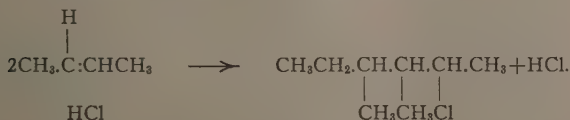


Four reactions are possible for the formation of the secondary product in the α -butylene reaction.



The compound contained in this secondary reaction was shown to decompose very readily into hydrogen chloride and a hydrocarbon. In the products of reactions (b) and (d) it will be noticed that the chlorine atom is attached to a carbon atom in the main chain—a stable configuration. The 3-chlor-methyl heptane produced in reaction (c) has its chlorine on a primary carbon atom. This is also stable. This leaves only reaction (a). In 3-methyl-4-chlormethyl hexane, the chlorine is attached to a carbon atom in a side chain, which is also adjacent to a methyl group. This has been proved to be an unstable configuration. Thus it is likely that 3-methyl-4-chloromethyl hexane is the chloride produced in the secondary reaction.

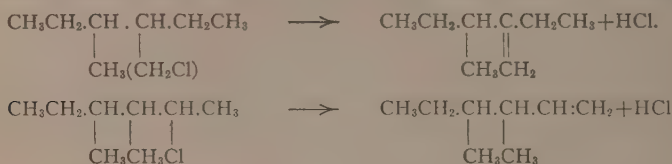
For the β -reaction there is only one possibility:



This substance ought not to be decomposed as easily as the 3-methyl-4-chlormethyl hexane mentioned. This agrees again with the experimental result, in that the product of the reaction was much more stable than the chloride produced in the case of the α -butylene. The secondary product is 2-chlor-3,4-dimethyl hexane.

In the γ -reaction, no secondary product was produced. It is likely that, should such a product have formed, it immediately would have decomposed again into either butylene and hydrogen chloride, or butylene and tertiary butyl chloride.

Since in the secondary reactions the chlorides produced were unstable, it is likely that the octylene hydrocarbons found present were formed from the chlorides, rather than the reverse. The reactions may be represented thus,



The hydrocarbon found present in the reaction with the α -compound was therefore likely to be 2-ethyl-3-methyl pentene, and that produced in the case of the β -compound, 3, 4-dimethyl hexene.

Should the hydrocarbons have been produced previous to the octyl chlorides, compounds with four-membered rings would have been necessary to explain their formation. Since these are very unstable, and since the compounds produced were stable, the possibility was discarded.

It was shown six years ago (7) that the relative rates of reaction of ethylene and propylene with hydrogen halides, could be used for their separation. The same applies to the butylenes. If hydrogen chloride is passed into a mixture of the butylenes at -78°C ., the γ -butylene is completely changed into the chloride, without either of the other butylenes being affected.

The α - and β -butylenes also differ in their rate of reaction, and since in the initial stages very little secondary product is formed, the rate at which hydrogen chloride is acted upon may be used as a method of estimating the relative amounts of the various butylene isomers in a mixture.

References

1. COFFIN, C. C. and MAASS, O. J. Am. Chem. Soc. 50:1427-1437. 1928.
2. COFFIN, C. C. and MAASS, O. Trans. Roy. Soc. Can. III, 21: 33-40. 1927.
3. MAASS, O. and RUSSEL, J. J. Am. Chem. Soc. 40:1561-1573, 1918; 43:1227-1230. 1921.
4. MAASS, O., BOOMER, E. H. and MORRISON, D. M. J. Am. Chem. Soc. 45: 1433-1438. 1923.
5. MAASS, O. J. Franklin Inst. 198(2): 145-159. 1924.
6. MAASS, O. and SIVERTZ, C. J. Am. Chem. Soc. 47:2883-2891. 1925.
7. MAASS, O. and WRIGHT, C. H. J. Am. Chem. Soc. 46: 2664-2673. 1924.
8. SUTHERLAND, B. P. and MAASS, O. Trans. Roy. Soc. Can. III, 20: 499-505. 1926.

SPECTROSCOPY OF THE LIGHT FROM THE NIGHT SKY¹

By J. C. McLENNAN², F.R.S., AND H. J. C. IRETON³, M.A.

Abstract

This paper describes the development and the construction, with optical details, of a high light power spectrograph suitable for the photography of the spectrum of the light of the moonless night sky and the spectra of auroral displays.

Preliminary experiments carried out with it in England and in Canada are described. Typical spectrograms recorded by the instrument are shown.

Suggestions for still further increasing the efficiency of the spectrograph are made. The advantages of using the spectrograph described are pointed out. Additional investigations of auroral phenomena, and an extension of those previously made are outlined.

Introduction

Some two years ago the writers with the collaboration of Dr. J. H. McLeod made a series of observations on the intensity of the light from the night sky corresponding to the green line of the spectrum of the non-polar aurora. Observations were made at Toronto, Ontario, and at Esterhazy, Saskatchewan, in Canada, and also with the kind assistance of Dr. Slipher at the Observatory in Flagstaff, Arizona, U.S.A.

These observations were made on moonless nights, when the sky was cloudless or not more than slightly overcast. The results showed that while the intensity of the light investigated exhibited small and not readily explainable fluctuations it gradually increased to a maximum value about an hour after midnight and then fell off again with the lapse of time to sunrise.

A similar variation in intensity was observed by Lord Rayleigh in an investigation carried out independently of our work, and practically concurrently with it. In our investigation we used a spectrograph and the photographic method while he used a photo-electric cell in measuring the intensity of the light. Lord Rayleigh, in his early work, found that the intensity of the light nearly always increased between nightfall and midnight, and his later observations, just recently described and published, have led him to conclude and state that the reality of this midnight maximum was now well established as a characteristic feature of the radiation from the night sky.

From the results achieved we have been encouraged to extend our spectrographic observations. In particular we hope from intensity measurements made with the spectrograph to clear up some problems still outstanding and connected with the origin of the non-polar auroral green line radiation from the moonless night sky. We also hope from observations on the

¹ Manuscript received March 18, 1930.

Contribution from the Physical Laboratory of the University of Toronto, Toronto, Canada, with financial assistance from the National Research Council of Canada.

² Professor of Physics and Director of the Physical Laboratory, University of Toronto.

³ Lecturer, Department of Physics, University of Toronto.

intensities of the different lines recorded in the spectra of the light from the polar aurora to gain some information of value on the distribution in the upper atmosphere of the elemental gases contributing to the emission of this light.

Recently we made an effort to shorten the time required to photograph the non-polar green line radiation from the cloudless sky on moonless nights, and with the help and co-operation of Mr. Frank Twyman, F.R.S., of The Adam Hilger Company, we have succeeded in producing an instrument with which, at sea level, we can obtain easily perceptible photographs of the green spectral line representing the non-polar auroral radiation in 10 to 20 minutes and well-marked ones in half an hour.

The Night Sky Spectrograph

The design of the night sky spectrograph developed will be seen from the sketches given in Fig. 1. The dispersion is obtained by the use of a 60° prism. The design called for a prism to have a length of face 85 mm. and a height

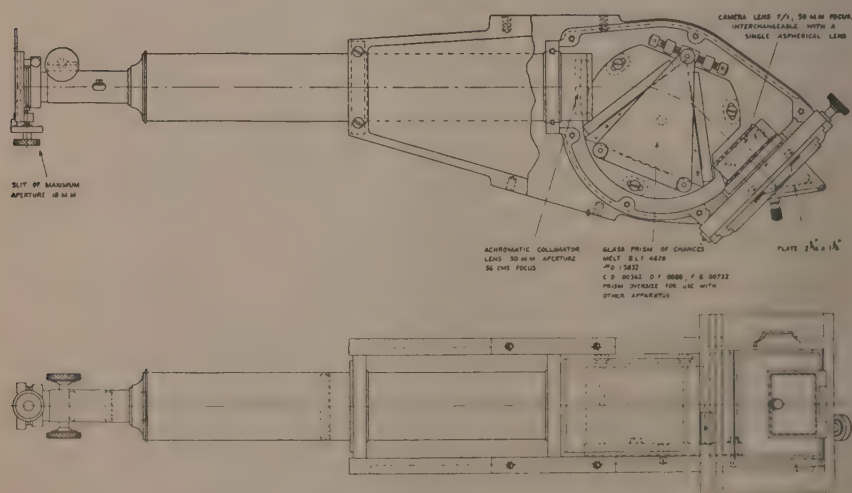


FIG. 1. Sectional elevation and plan view of the night sky spectrograph.

52 mm., but the one actually used in the instrument was a prism that was available in stock. It had a length of face 127 mm. and a height 75 mm. It was made by Messrs. Chance from glass of melt No. B.L.F. 4628, the refractive indices for which as given by the maker were:

$$\mu_C = 1.57958$$

$$\mu_D = 1.58320$$

$$\mu_F = 1.59200$$

$$\mu_G = 1.59932$$

The collimator lens was an achromatic cemented doublet of 50 mm. aperture and 56 cm. focus. The slit could be varied by means of an aperture wedge and had a maximum effective length of 18 mm. It was mounted in a draw

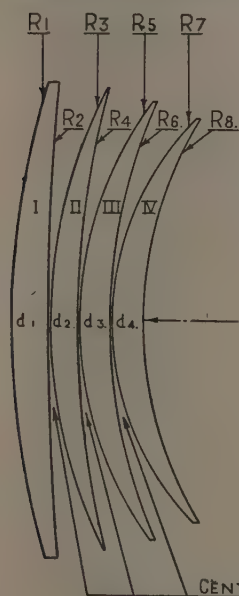


FIG. 2. 2" F/1.0. Lens. T. Smith's Formula

tube having a 50 mm. rack and pinion focussing motion. We had two interchangeable camera lenses, one consisting of a single aspherical lens designed to give the maximum concentration of light for the mercury green line only and the other an F/1 lens of 50 mm. focus, designed to give good focus of the entire spectrum on a flat but tilted plate. Two plate holders were provided, one taking plates approximately 108 mm. $\times$ 82.5 mm. for use with the single aspherical lens and the other taking small plates 60 mm. $\times$ 45 mm. tilted at an angle necessary for the photographing of the entire spectrum.

The experiments described in this paper are limited to the ones obtained with the F/1 lens of 50 mm. focus. This compound lens had four components and was designed in accordance with a formula by Mr. T. Smith of the National Physical Laboratory, Teddington.

Fig. 2 and 3 illustrate its characteristic features. The focal lengths of the component lenses are as follows:

- Lens (1) 208.0 mm.
- Lens (2) 213.4 mm.
- Lens (3) 195.9 mm.
- Lens (4) 190.0 mm.

The angular field was about 10 degrees and the size of plate covered was 8.5 mm. diagonal.

The lens was constructed by Messrs. Ross in accordance with the results of the final calculations ordinarily made by them to adapt their lenses to the refractive indices of the glasses used. The refractive indices of the four glasses used for the mercury green line λ 5461 Å are as follows:

- (1) 1.61491
- (2) 1.58631
- (3) 1.61491
- (4) 1.58131

COMPUTED SPHERICAL ABERRATION
FOR F/1.0 APERTURE = 0.02%
UNDERCORRECTED.

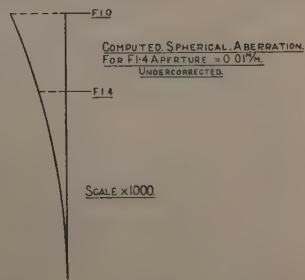


FIG. 3. Characteristic features of the F/1 lens used.

The residual spherical aberration over the whole of the aperture was removed by Messrs. Ross, the figuring being done with the lens *in situ* on a lens testing interferometer. The correction made to within a quarter of a wave-length was carried out with light of the mercury green line $\lambda 5461 \text{ \AA}$. The body of the spectrograph which enclosed the prism and lens and carried the collimator and camera plate holder was strongly constructed of aluminum. Two sets of holes tapped 5/16 inch Whitworth were provided on two sides of the instrument for mounting it to a tripod or other type of support. As actually used the instrument is shown in the mount in Fig. 4. The collimator, it will be seen, could be directed easily towards any point in the night sky. Large clamping nuts enabled one to clamp the instrument to its stand in any position selected.



FIG. 4 View of the complete night sky spectrograph.

Photographic Plates and Slit Width

In the course of our observations we tested out a number of types of photographic plates recommended to us as likely to be specially sensitive to light of wave-length $\lambda 5577 \text{ \AA}$, but the results obtained with most of them were very disappointing. Others such as Marion iso-record plates gave fair results, but the type that proved to be by far the most sensitive to the light of the auroral green line was that known as Cramer's iso-instantaneous plate. They were manufactured by The G. Cramer Dry Plate Company of St. Louis, U.S.A.

Tests made to ascertain the relation of slit width to the clearness with which the non-polar auroral green line could be photographed showed that best records were generally obtained when a slit width of 1 mm. was used.

Observation Stations

Observations were made with the night sky light spectrograph at three different and widely separated stations. The first was in England at Portnall House, the Dormy House of The Wentworth Golf Club, Virginia Water. The second was at Caledon, about 45 miles northwest of Toronto in Canada, where the elevation was about 425 metres above sea level. The third was on the top of Sulphur Mountain, near Banff, in Alberta, Canada. Here the elevation above sea level was about 2,300 metres.

Experiments at Portnall House

The experiments at Portnall House, Wentworth Golf Club, Virginia Water, England, were carried out during the period between August 27 and September 21, 1929. The distance of Portnall House from London was about 25 miles. To the north of it was Windsor Park and to the west and

southwest was Chobham Common. Portnall House, which was to the east of our observation station, was concealed from it by trees and by a high and extended dense clump of rhododendron bushes. From this observation station on clear moonless nights the sky to the north, west, and south was quite free from illumination by industrial or street and house lights. Light reflected from the city of London itself could only be seen faintly on the horizon in the far east from Portnall House, but not from the observation station. Nearly all the photographs taken at this station were obtained with the spectrograph pointing at an elevation of 60° or 70° and in a direction slightly south of west. Before commencing this series of observations the spectrograph was adjusted with the greatest care. With the adjustments made we were satisfied that spectrograms recorded on the same or successive nights could be compared as to relative intensity with every confidence. Before and after each plate was exposed to the light of the night sky comparison spectra were recorded on it of the light from an alcohol lamp fed with sodium iodide held on a small platinum coil sealed to a glass rod. This served admirably to calibrate our spectrograms. Exposures were made on many nights and under a variety of conditions. A few illustrations of the results obtained follow:

I. The reproductions of the auroral green line $\lambda 5577 \text{ \AA}$ designated by A, B and C on Plate I were obtained with a Cramer iso-instantaneous plate on the night of September 9-10. For A the exposure was one hour from 9.30 to 10.30 p.m., for B two hours from 10.30 p.m. to 12.30 a.m., and for C four hours from 12.30 a.m. to 4.30 a.m. The enlargement in each case was 27 times. The sky was moonless, the moon having set at 9.30 p.m. Reproduction D on Plate I was obtained on a moonless night, September 4-5, with seven hours exposure, but the photographic plate used in this case was a Marion iso-record one. These reproductions on Plate I serve to demonstrate the superiority of the Cramer iso-instantaneous plates for night sky light spectrography. For all four of the spectrograms the slit width used, it may be stated, was 1 mm.

II. On the nights of September 10-11 and 12-13 some spectrograms were taken with the object of ascertaining the shortest time of exposure required to obtain a visibly perceptible record of the non-polar auroral green spectral line with the light from the moonless night sky. Reproductions A, B, C, Plate II, were from spectrograms taken on the 10-11, and those designated D, E and F, Plate II, from spectrograms taken on the 12-13. The enlargement in all cases is five-fold. A was obtained with an exposure of one hour, namely from 9.30 p.m. to 10.30 p.m., B with an exposure of 40 minutes, from 10.30 p.m. to 11.10 p.m., and C with an exposure of 20 minutes, from 11.10 p.m. to 11.30 p.m. The moon set at 10 p.m. D was taken with an exposure of 85 minutes, extending from 1.25 to 2.50 a.m., E with an exposure of 40 minutes, from 12.45 a.m. to 1.25 a.m., and F with an exposure of 20 minutes from 12.25 to 12.45 a.m. A number of 10 and 15-minute exposures were made on each of the evenings mentioned above but no visible record of the auroral green line was obtained with any of them. It must be stated here that the moon set at 11.51 p.m. on the twelfth and that with all six spectrograms shown on Plate II

the slit width used was 1 mm. From the reproductions shown on Plate II it is clear that it should be possible with our spectrograph to make comparisons of the intensity of the green line radiation from the moonless night sky at various times during a single night. Exposures of 20 to 25 minutes in the south of England should suffice. It is clear, too, that within narrow limits, comparisons could also be made with this spectrograph of the intensity of the green line radiation at any selected time on different moonless nights.

III. Plate III shows reproductions marked A and B each enlarged 27 times of a spectrogram taken with an exposure of 40 minutes on the night of September 13-14 while the moon, which did not set until 12.41 a.m. on the 14th, was still above the horizon. A was obtained between 9.30 p.m. and 10.10 p.m. with a slit width of 0.5 mm., and B between 10.10 p.m. and 10.50 p.m. with a slit width of 1 mm. These and other photographs of a similar kind showed that practically nothing was to be lost in intensity and definition by the use of a slit width as great as 1 mm. Both A and B, it will be seen, showed in addition to the line $\lambda 5577 \text{ \AA}$ a broad band on the short wavelength side of it. This band was always obtained with the light from the moonlit sky and was due to sunlight reflected to the earth by the moon. On most of the spectrograms which showed this band the H and K solar absorption lines were clearly marked.

IV. Plate IV shows reproductions of other spectrograms taken on the night of September 13-14 with a slit width of 1 mm. As already stated the moon set at 12.41 a.m. on the 14th. A, taken between 10.10 p.m. and 10.50 p.m., shows the line $\lambda 5577 \text{ \AA}$ and the solar band both well marked. B, taken between 10.50 p.m. and 11.30 p.m., shows the spectral line $\lambda 5577 \text{ \AA}$ clearly marked but the solar band which was present had considerably lessened intensity. In C, which was taken between 11.40 p.m. and 12.20 a.m., the green auroral line is still well marked but the solar band is scarcely detectable. D was taken with an exposure of one hour between 12.20 a.m. and 1.20 a.m. on the 14th. It shows the line $\lambda 5577 \text{ \AA}$ well marked but the solar band is entirely absent. This set of reproductions illustrates very clearly the contribution made by moonlight to the character and strength of the spectrograms taken of the night sky radiation.

V. Plate V shows a set of five spectrograms taken of the auroral green line radiation from the moonless night sky on September 10-11. Each exposure was of one hour's duration and the width of slit used was 1 mm. The moon set at about 10 o'clock on the 10th. The exposure for A was from 11.45 p.m. on the 10th to 12.45 a.m. on the 11th, for B from 12.45 a.m. to 1.45 a.m., for C from 1.45 a.m. to 2.45 a.m., for D from 2.45 a.m. to 3.45 a.m., and for E from 3.45 a.m. to 4.45 a.m. Tracings taken with a Moll spectrophotometer showed that of the five spectral lines recorded, that obtained for the period 1.45 a.m. to 2.45 a.m., namely C, was the strongest. As the times recorded in this paper were in the season of the year when the Daylight Saving Bill was in operation the records shown on Plate V would go to support the

view already put forward by McLennan, Ireton and McLeod and by Lord Rayleigh that the non-polar auroral green line radiation from the moonless night sky acquires a maximum intensity shortly after midnight.

Experiments at Caledon, Ontario.

On two occasions we were given an opportunity of taking photographs of the spectrum of the radiation from the night sky at Caledon. One of these was the night of October 7, 1929. On the evening of this night the sun set at 5.50 p.m. and the moon at 8.18 p.m. Early in the evening there was a feeble auroral display consisting of a general illumination of the northern sky coupled with occasional streamers shot up towards the zenith. Our first exposure was made at 9.30 p.m. and lasted for half an hour. The instrument was pointed towards the north and was given an elevation of about 75° . The slit width used was 0.5 mm. A reproduction of the spectrogram obtained is shown enlarged 27 times at A in Plate VI. The auroral line at $\lambda 5577 \text{ \AA}$ is clearly recorded, and in addition the first negative bands of nitrogen at $\lambda 3914 \text{ \AA}$ and $\lambda 4278 \text{ \AA}$ are well marked. Two additional spectrograms B and C were taken, the first with a one-hour exposure beginning at 10.00 p.m. and the second with a two-hour exposure beginning at 11.00 p.m. The slit width used in both cases was 1 mm. While these spectrograms were being taken the general auroral illumination appeared to be somewhat less than it was during the exposure for spectrogram A, but auroral streamers continued to be projected across the sky at intervals. The fourth spectrogram, D, on Plate VI, was taken with an exposure of four hours beginning at 1.00 a.m. on the morning of October 8. The spectrogram shows both the auroral green line $\lambda 5577 \text{ \AA}$ and the nitrogen band $\lambda 3914 \text{ \AA}$. In addition there is a broad continuous band shown between them. It was probably due to the morning twilight as the sun rose that day at 6.23 a.m.

On a second occasion, the evening of November 30, 1929, a series of spectrograms was taken with the object of determining the least time of exposure required to secure definite visibly perceptible photographic records of the non-polar auroral green line radiation from the night sky. The results are shown in Plate VII. Reproduction A, enlarged five times, was obtained with an exposure of 40 minutes, beginning at 12.50 a.m. December 1. Reproduction B is the record obtained with an exposure of 30 minutes beginning at 1.20 a.m., and reproduction C was obtained with an exposure of 20 minutes beginning at 1.40 a.m. The record of the green line is quite clear in reproductions A and B, but is only just detectable in reproduction C. With exposures of 15 minutes and of ten minutes we could obtain no visible record of the line on the plates.

From the observations made at Caledon, two conclusions can be drawn. In the first place it seems to be demonstrated that the green line radiation from the moonless night sky at Caledon is practically of the same intensity as it is at Virginia Water, in Surrey, England. At both places it required an exposure of 20 minutes to obtain a clearly visible spectral record of the auroral green line

radiation. In the second place it is clear that with the spectrograph we developed, it will be easily possible to obtain spectrograms of the light of the polar aurorae with exposures of considerably less than half an hour's duration. It would seem that an exposure of ten minutes or even less should suffice. It will be possible then in the future when polar auroral displays occur to obtain spectrograms of the light originating in the display at different heights. This should open up a way for gaining information on the distribution with height of the oxygen and the nitrogen that emit the radiation in the upper atmosphere.

Experiments at Sulphur Mountain, Banff, Alberta, Canada.

Through the courtesy of Mr. J. Patterson, Director of the Meteorological Service of Canada, we were given an opportunity of making with the kind help and co-operation of Mr. N. B. Sanson, some observations at the meteorological station situated on Sulphur Mountain, near Banff. This station is at an elevation of about 2,300 metres.

A number of spectrograms of the light of the moonless night sky were obtained during the period between October 31 and November 5 inclusive. All exposures were begun after the time of evening twilight and ended before the time of morning twilight. In noting the times account was taken of the elevation of the observing station above sea level.

Illustrations of the spectrograms obtained at this station are shown in Plates VIII to XIV, and an examination of them will show that the wave-length $\lambda 5577 \text{ \AA}$ was recorded on every spectrogram. It will be seen too that the characteristic nitrogen bands of the polar aurora at $\lambda 4278 \text{ \AA}$ and $\lambda 3914 \text{ \AA}$ were recorded in many cases. These bands were obtained even when the existence of a polar auroral display was not detectable visually. An account of the results obtained is given in detail below.

All observations were made with the spectrograph previously described in this paper. The width of the slit was always 1 mm., unless otherwise stated.

I. Plates VIII and IX contain reproductions of the spectra obtained on the night of October 30. Plate VIII, A, B, and C shows a five-fold enlargement of spectrograms obtained for consecutive exposures of 10, 15, and 20 minutes respectively. The first exposure began at 7.30 p.m., the moon having set at 4.47 p.m., and the sun at 5.19 p.m. In each of the three spectrograms the auroral green line is recorded, and in addition the nitrogen band at $\lambda 3914 \text{ \AA}$, the latter being rather faint. During the same evening another series of exposures was made, the results obtained are shown opposite A, B, C, D, and E in Plate IX. They have been enlarged approximately 27 times. A corresponds to an exposure time of 60 minutes, beginning at 8.15 p.m. B, C, D, and E are illustrations of the spectrograms obtained when the successive exposure times were 40 minutes, 60 minutes, two hours, and 3.5 hours respectively. The 3.5-hour exposure ended at 4.25 a.m. The collimator of the spectrograph was directed towards the pole star for these exposures. The brightness of the sky appeared to remain constant throughout the night, and there was almost a complete absence of clouds.

As to the spectrograms on Plate IX they all show the auroral green line. The nitrogen band at $\lambda 3914 \text{ \AA}$ can be readily seen on spectrograms C, D and E, and it is just detectable on A and B. The band $\lambda 4278 \text{ \AA}$ appears faintly on spectrograms C, D, and E.

It is clear from the records shown on Plates VIII and IX that there was a display of the polar aurora throughout the whole period during which observations were made. Visual observation however did not reveal any perceptible display. A point that may have some interest in connection with the spectrograms in Plates VIII and IX is the approximately constant ratio that appeared to exist between the intensity of the auroral green line radiation and that of the radiation corresponding to the nitrogen band at $\lambda 3914 \text{ \AA}$.

II. Some exposures of comparatively short duration were made during the night of November 3. Reproductions of four of the spectrograms obtained are shown in Plate X. The exposure which gave spectrum A began at 7.30 p.m., and lasted for ten minutes. The collimator of the spectrograph was pointed in the direction of the North Star. The sky was clear and free from clouds. No polar aurora was visible. The spectrograms B, C and D were obtained with three consecutive exposures, the first of which began at 1.30 a.m. November 4. The times of exposure were 10, 15, and 20 minutes respectively. The presence of floating clouds made it necessary to point the spectrograph to different portions of the sky for these different exposures. Spectrograms B and D were obtained when the spectrograph was directed towards the north at an elevation midway between the pole star and the zenith. When spectrogram C was recorded the spectrograph was pointed in the direction of the constellation Pleiades. A careful examination of the plates, and the reproductions made from them, showed that spectrogram A differed from the other spectrograms shown in Plate X in one important respect. No trace of the nitrogen band $\lambda 3914 \text{ \AA}$ can be observed in it, whereas in all the others it appears distinctly. The absence of the nitrogen bands in spectrogram A indicates that while the photograph was being recorded there evidently was no polar auroral display such as was no doubt responsible for the presence of the nitrogen bands in the spectrograms B, C, and D. The record of the radiation at $\lambda 5577 \text{ \AA}$ in spectrogram A was due to the light from the moonless sky only. Such a conclusion seems justifiable too when it is pointed out that spectrogram A was taken at 7.15 p.m., whereas the others were recorded at a time at least five hours later.

It would seem therefore reasonable to state that a clearly defined spectral line of wave-length $\lambda 5577 \text{ \AA}$ corresponding to the radiation of the green light of the night sky was photographed at the Sulphur Mountain Station with our spectrograph in as short a time as 15 minutes.

III. In an attempt to repeat the experiments, and to confirm the conclusions of the authors and Lord Rayleigh which led them to state that the intensity of the light of the night sky reached a maximum at about an hour after midnight, a series of six consecutive exposures each 1.5 hours long was made on the night

of November 4. The first exposure began at 7.45 p.m. and the sixth ended at 4.25 a.m., November 5. Reproductions of the spectrograms obtained are shown in Plate XI A to F. Spectrogram A is the first of the series. The sky however did not remain sufficiently clear and free from clouds to warrant our drawing any definite conclusions from the spectrograms obtained in regard to that portion of the radiation from the night sky that was non-polar in origin. It is clear from the reproductions shown that a considerable polar auroral display must have existed throughout the complete period of the exposures. No display however was evident with naked eye observation, except perhaps about midnight when there appeared to be a slight increase in the general brightness of the sky in a northerly direction.

IV. During the early portion of the night of November 5, three short exposures were made. The first one began at 7.30 p.m. and lasted for ten minutes. The second began at 7.40 p.m. and lasted for 15 minutes, while the third began at 7.55 and lasted for 20 minutes.

Reproductions of the spectrograms obtained are shown in Plate XII A, B, and C. It will be seen that each of them shows the wave-length at $\lambda 5577 \text{ \AA}$ and no other wave-lengths. Spectrogram A which was obtained in ten minutes, shows the line $\lambda 5577 \text{ \AA}$ faintly but quite definitely. It is clear therefore that we were able to record the radiation from the moonless night sky on Sulphur Mountain in as short a time as ten minutes.

V. The spectrograms A, B and C shown in Plate XIII were obtained also on the night of November 5.

They constitute a rather interesting series in their relations to the spectrograms shown in Plate XII taken just previously on the same night. The exposure for spectrogram A began at 8.15 p.m., and ended at 9.30 p.m., that for spectrogram B began at 9.30 p.m., and ended at 10.45 p.m. The exposure for spectrogram C was from 10.45 p.m. to 12 midnight. It will be seen that in all the spectrograms A, B, and C, the intensity of the auroral green line remained practically constant. In spectrogram A an exceedingly faint trace of the nitrogen band $\lambda 3914 \text{ \AA}$ can be seen. In spectrogram B it is more clearly marked, while in spectrogram C it is quite strong, and the nitrogen band at $\lambda 4278 \text{ \AA}$ is recorded with moderate intensity as well.

It is evident from features characterising the spectrograms in Plate XII and Plate XIII that earlier than 8.15 p.m. the sky was entirely free from polar aurorae, and that at some time after 8.15 p.m., a polar auroral display began and continued with a gradually increased intensity, reaching a maximum value at midnight when it became necessary to discontinue the observations. The faintness of the display in its early stages is evidenced from the fact that even with an exposure of an hour and a quarter the nitrogen band $\lambda 3914 \text{ \AA}$ could only just be detected in the original of spectrogram A of Plate XIII.

VI. On the night of November 2, a very definite auroral display was observed as early as 7 p.m. and it continued with varying intensity throughout the night. The type displayed was characterised by a general intense

illumination extending over the whole northern half of the sky. Superimposed on this bright background occasional streamers shot up from the horizon towards the zenith. They could be observed at various times in different positions over an arc extending from the northwest to the northeast. None of these streamers appeared to have a duration of more than a few minutes.

It seemed that it would be of interest to take spectrograms of the display using various widths of the slit of the spectrograph and different times of exposure. The spectrograms recorded are shown in Plates XIV and XV, A to H inclusive. Spectrogram A was taken when the slit width was 0.2 mm., and the length of exposure was 25 minutes. The exposure began at 7.05 p.m., the time of sunset for November 2 being 5.08 p.m. Spectrogram B was taken when the slit width was 0.5 mm., and the length of exposure was 30 minutes. This exposure began at 7.30 p.m. Spectrogram C was taken when the slit width was 0.05 mm., and the exposure time which ended at 8.30 p.m. was 60 minutes. For the spectrograms D to H the slit was kept fixed at a width of 1 mm., and the exposures were made in succession, the first one beginning at 3.08 a.m., November 3. The times of exposure for the spectrograms of the series from D to H were 10, 15, 20, 30 and 5 minutes respectively. The last exposure was completed at 4.30 a.m., November 3. All exposures were made with the spectrograph pointing to the north star.

In all the spectrograms in Plates XIV and XV the auroral green line $\lambda 5577 \text{ \AA}$, the nitrogen band $\lambda 4278 \text{ \AA}$ and the nitrogen band $\lambda 3914 \text{ \AA}$ are distinctly recorded. An examination of the original plate shows that in spectrograms E, F, and G, six other bands were recorded. These can be detected in the reproduction of spectrogram G. The positions of these bands in the spectrogram are indicated by arrows.

The photographs of the auroral display obtained indicate that it should be possible to photograph the spectra of aurorae with very short exposures and with quite narrow slits with our spectrograph. It should therefore be possible to take spectrograms which could be used to compare the spectra given out by different regions of an auroral display. It should also be possible by the use of this spectrograph to obtain spectrograms which would give considerable information regarding the details of the structure of auroral spectra of different types.

As already stated by us the experiments described in this paper were limited to the ones obtained with the compound F/1 lens of 50 mm. focus. In a second communication we intend to give the results of our observations with a camera lens consisting of a single component designed to give a maximum concentration of light for the auroral green line. It is highly probable that we shall be able by the use of this lens to reduce exposures by as much as 30% in taking spectrograms of auroral green line radiation.

Summary of Results

1. With the high light power spectrograph developed by us and described in this paper, it is possible to obtain photographs of either the spectrum of the radiation of the moonless night sky at sea level or the spectrum of the light of an auroral display in a considerably less time than heretofore.

2. Exposures made with different types of photographic plates showed that Cramer iso-instantaneous plates were much superior to all others tested for the photography of the light from the moonless and cloudless night sky.

3. From the photographs taken at Virginia Water, Surrey, England, and at Caledon, Ontario, Canada, it can be seen that easily perceptible photographic records of the non-polar auroral green line $\lambda 5577 \text{ \AA}$ can be obtained in 20 minutes. The intensity of this radiation at these two widely separated stations seemed to be about the same.

4. It was found that at the elevation of the observing station on Sulphur Mountain, Banff, Alberta, Canada, it was possible to photograph the spectrum of the radiation of the moonless night sky corresponding to $\lambda 5577 \text{ \AA}$ in as short a time as ten minutes.

5. Clear photographs of the spectrum of the light of the polar aurora showing six spectral lines in addition to the oxygen green line $\lambda 5577 \text{ \AA}$ and the nitrogen bands $\lambda 3914 \text{ \AA}$ and $\lambda 4278 \text{ \AA}$ were obtained with exposures of a quarter to half an hour, when a slit 1 mm. in width was used.

6. From the reproductions of auroral spectra shown in this paper it will be seen that with spectrograms taken with the high light power spectrograph we have developed it will be easily possible to follow and record in any latitude variations occurring during a single night in the intensity of the non-polar auroral green line radiation from the moonless night sky. It will be possible too with this instrument to photograph frequently during its occurrence the spectrum of the light coming to us from different parts of an auroral display.

Acknowledgments

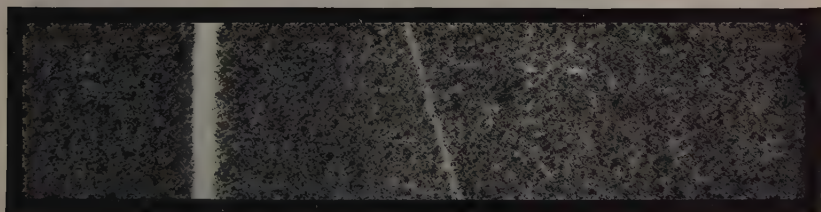
We wish to record our grateful thanks to Mr. A. M. I. A. W. Durnford for assistance in mounting the photographs, to Mr. A. Reading for help in making the enlargements, and to Mr. R. G. Campbell and Mr. R. Turnbull for their kind assistance in making observations; we wish to record too appreciation of the courteous treatment extended to us by the authorities of the Dormy House of the Wentworth Golf Club, Virginia Water, Surrey, England.

A

$\lambda 5577\text{\AA}$



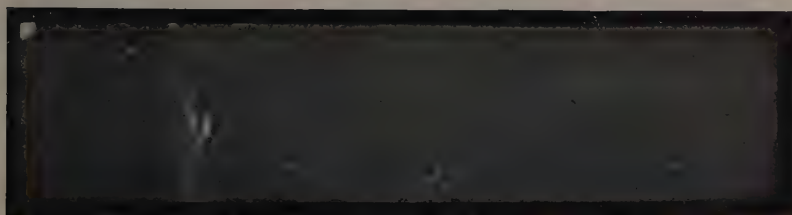
B



C



D



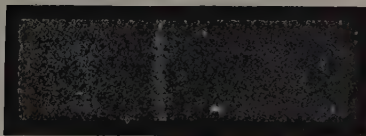
The auroral green line $\lambda 5577\text{\AA}$. Spectrograms taken at Virginia Water, England. The reproductions designated by A, B and C were obtained with a Cramer iso-instantaneous plate, that marked D was obtained with a Marion iso-record plate.

-λ5577A

A



B



C



D



E



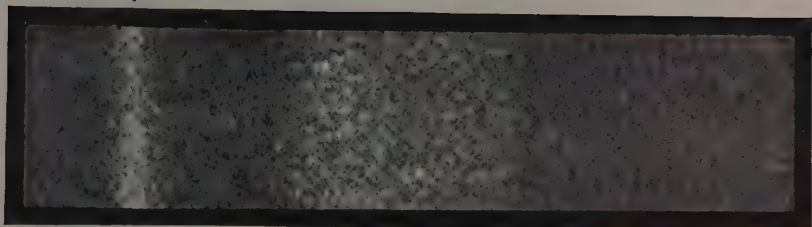
F



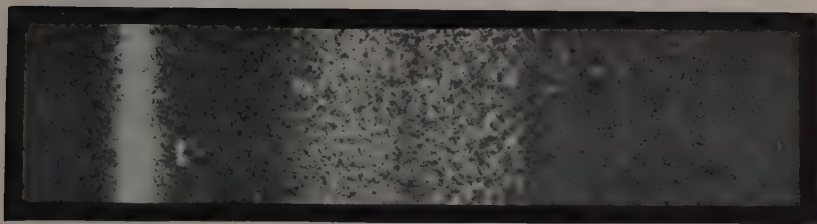
*Spectrograms taken at Virginia Water, England.
A, B, C were taken with exposures of 1 hr.,
40 min. and 20 min. respectively, spectro-
grams D, E, F with exposures of
85 min., 40 min. and 20 min.*

A

—A5577A

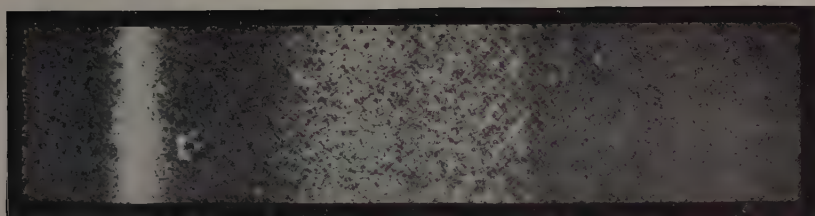


B



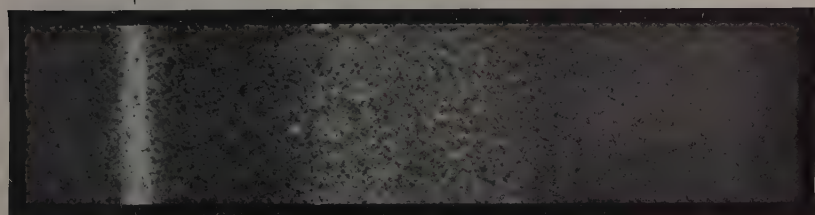
Spectrograms taken at Virginia Water, England, while the moon was still above the horizon, with an exposure of 40 min., and a slit width of 0.5 mm. and 1 mm. respectively.

A

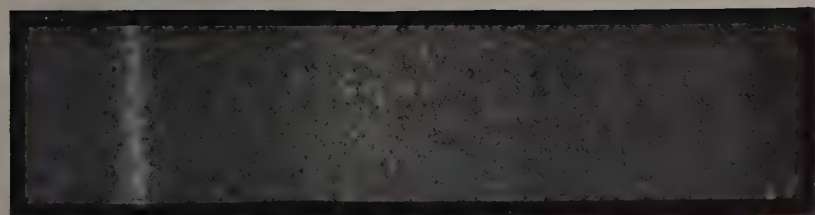


B

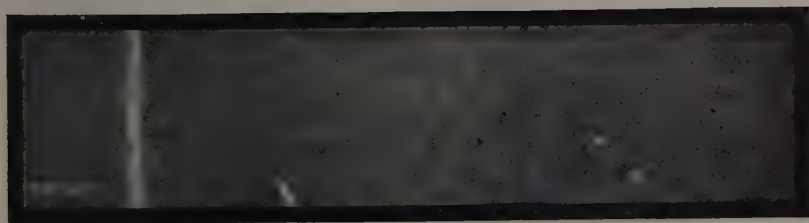
—λ5577A—



C

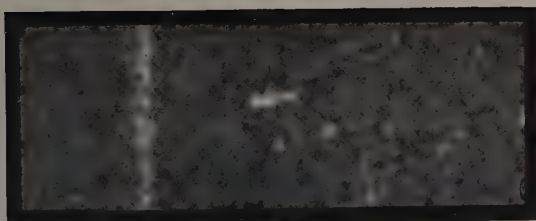


D

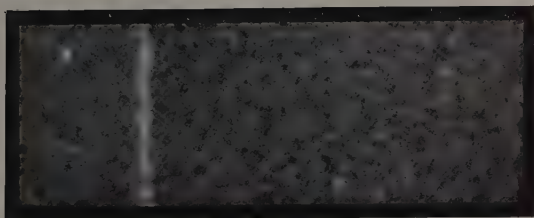


Spectrograms taken at Virginia Water, England. Illustration of the contribution made by moonlight to the character and strength of the spectrograms taken of the night sky radiation; slit width of 1 mm., exposure for A, B, C, 40 min. and 1 hr. for D.

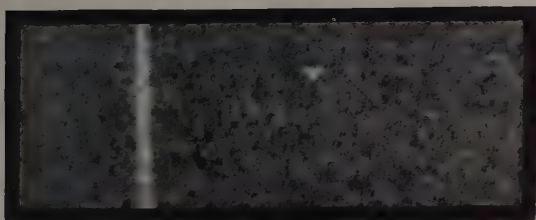
A



B



C



D



E



4577A

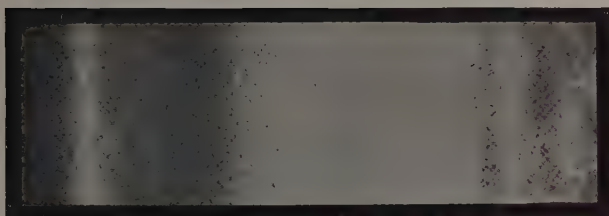
Spectrograms of the auroral green line radiation from the night sky taken at Virginia Water, England; exposure C, taken between 1.45 and 2.45 a.m., is the strongest line.

-λ 5577A

-λ 4278A

-λ 3914A

D



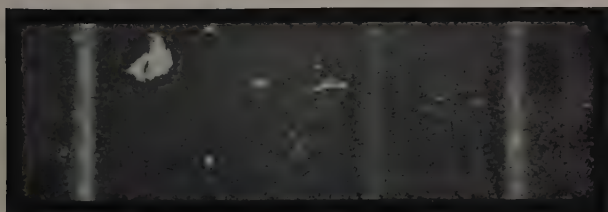
C



B



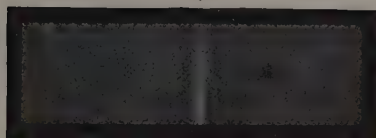
A



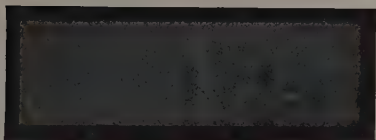
Spectrograms taken at Caledon, Ontario. Exposures: 0.5 hr. for A, 1 hr. for B, 2 hr. for C and 4 hr. for D.

—A 5577 A

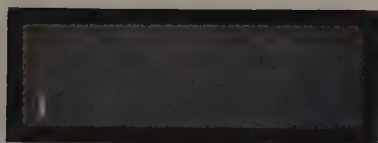
A



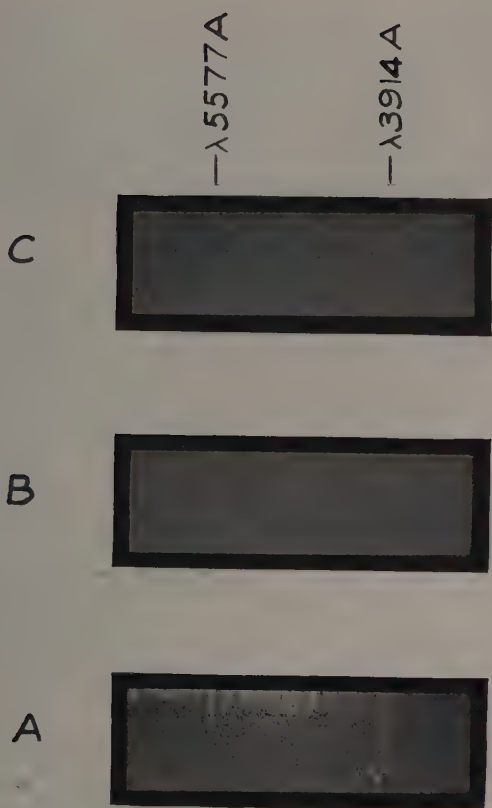
B



C



*Spectrograms taken at Caledon, Ontario.
Exposures: 40 min. for A, 30 min.
for B and 20 min. for C.*



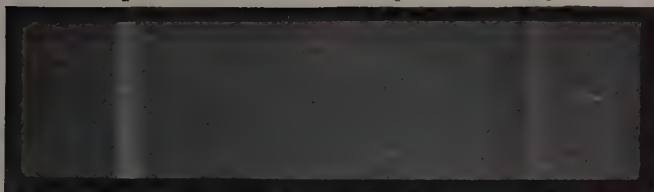
*Spectrograms taken at Sulphur Mountain,
Banff, Alberta, with exposures of 10,
15 and 20 min. respectively.*

—λ5577A

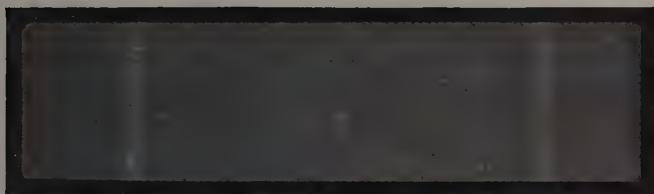
—λ4278A

—λ3914A

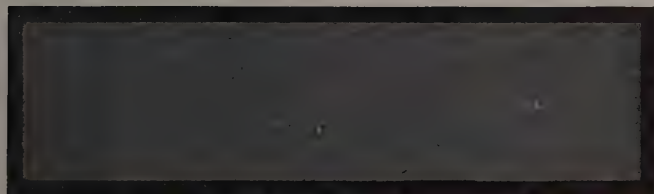
E



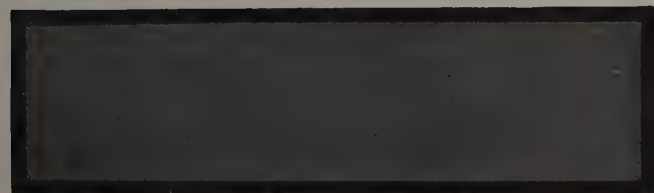
D



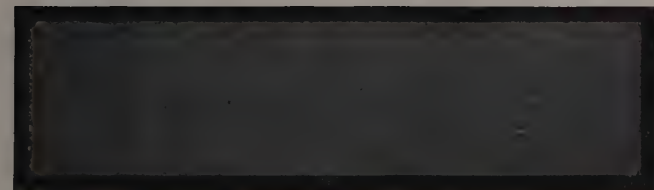
C



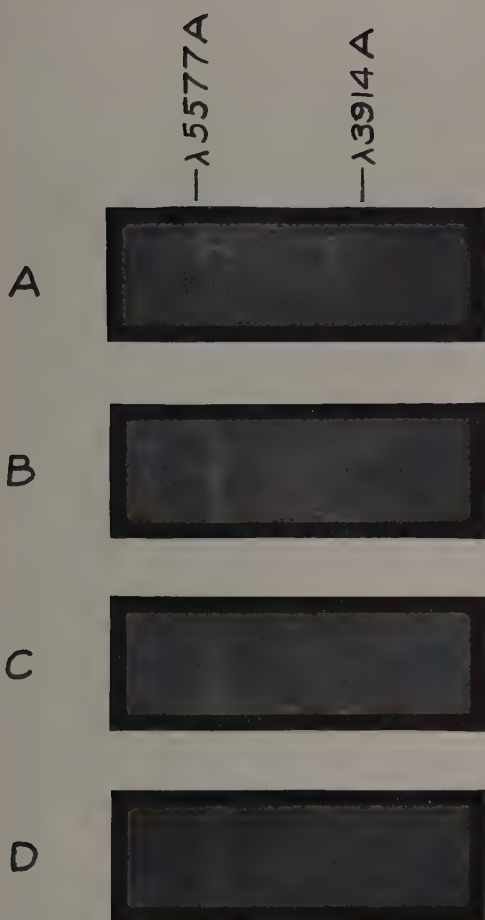
B



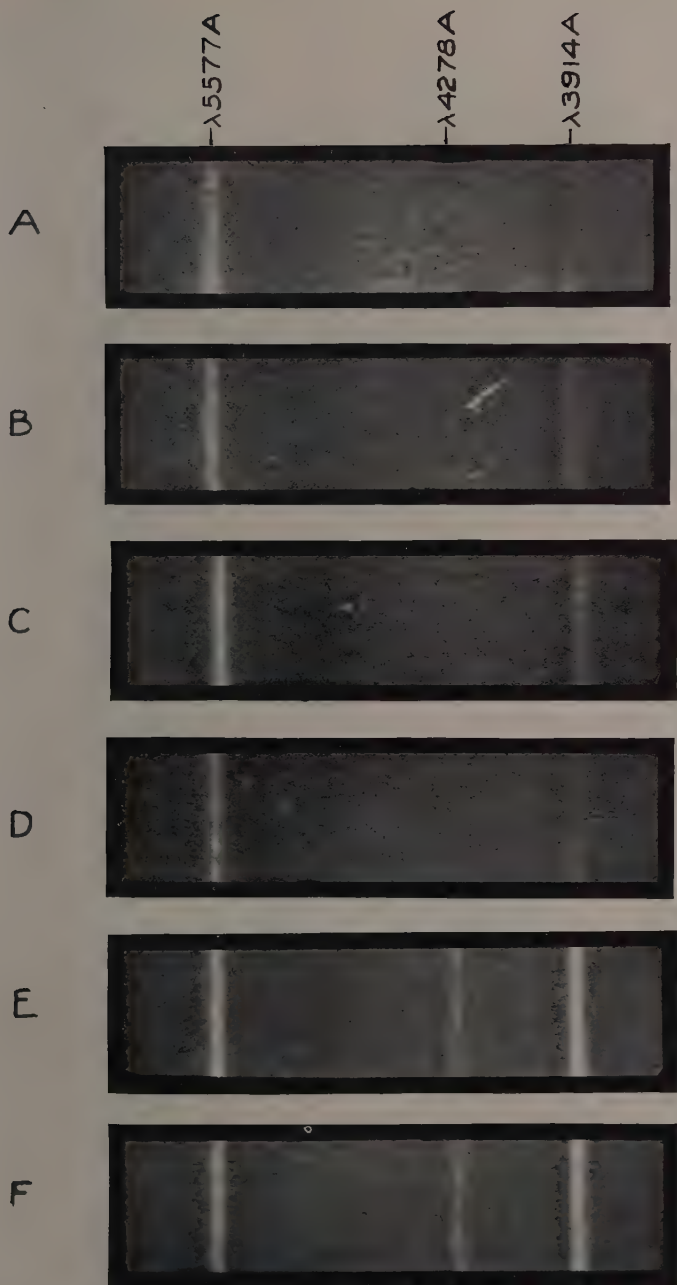
A



Spectrograms taken at Sulphur Mountain, Banff, Alberta, with exposures of 60 min., 40 min., 60 min., 2 hr. and 3.5 hr. respectively.



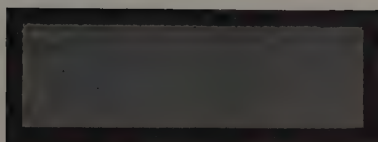
*Spectrograms taken at Sulphur Mountain,
Banff, Alberta, with exposures of 10,
10, 15 and 20 min. respectively.*



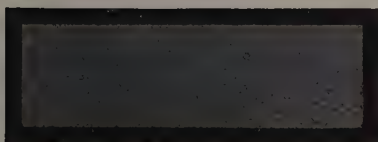
*Spectrograms taken at Sulphur Mountain, Banff, Alberta,
each exposure lasting 1.5 hr.*

—λ 5577A

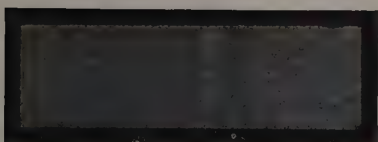
A



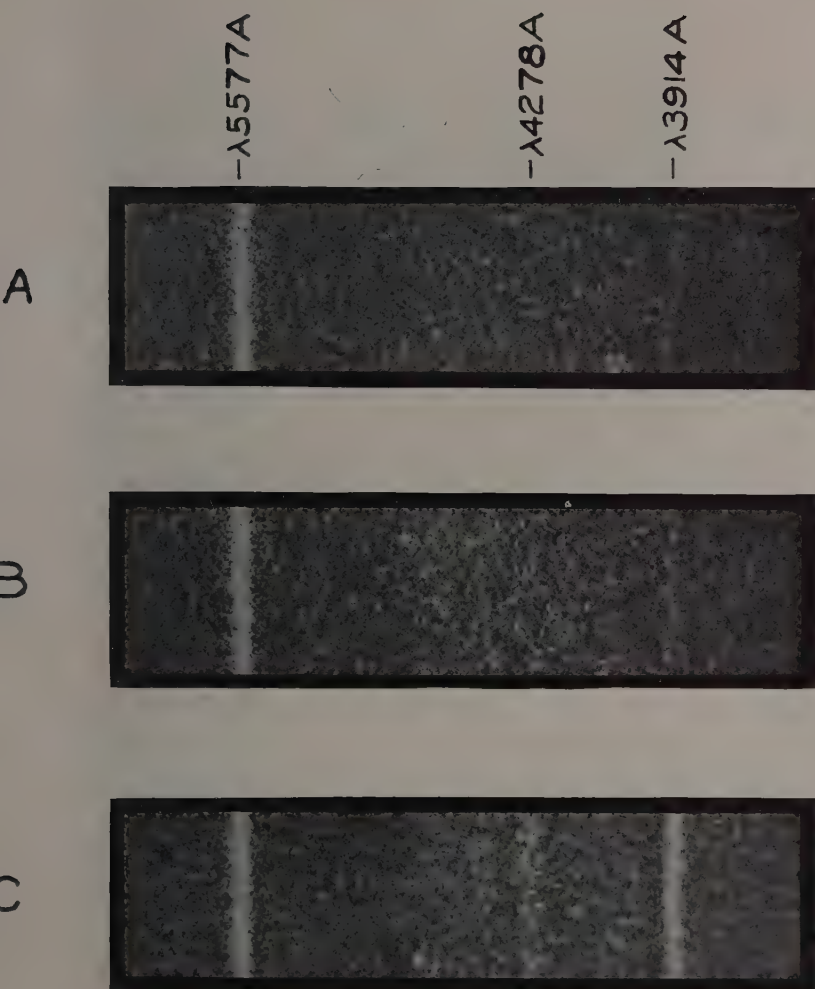
B



C



*Spectrograms taken at Sulphur Mountain,
Banff, Alberta, with exposures of 10,
15 and 20 min. respectively.*



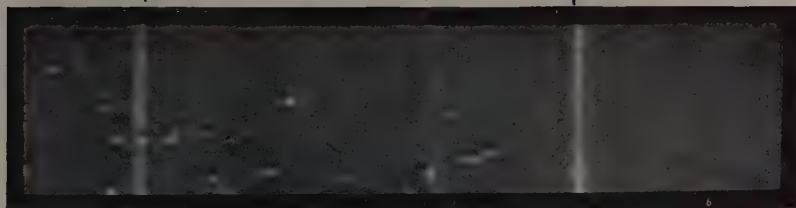
Spectrograms taken at Sulphur Mountain, Banff, Alberta, each exposure lasting 75 min.

A

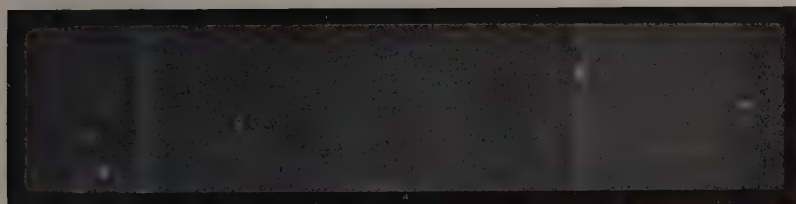
$\lambda 5577A$

$\lambda 4278A$

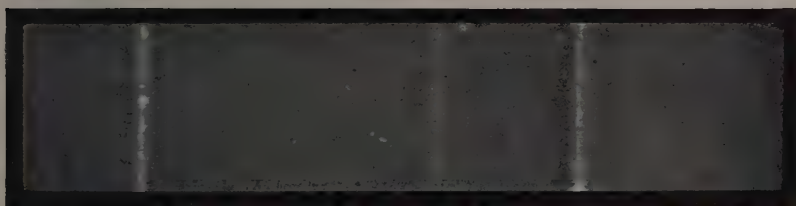
$\lambda 3914A$



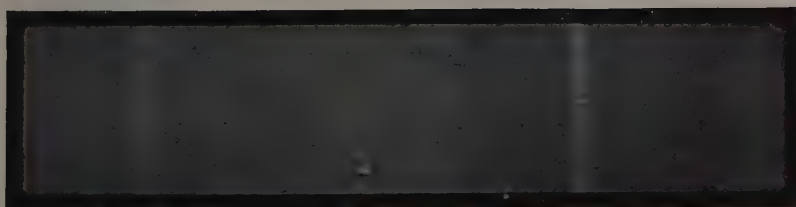
B



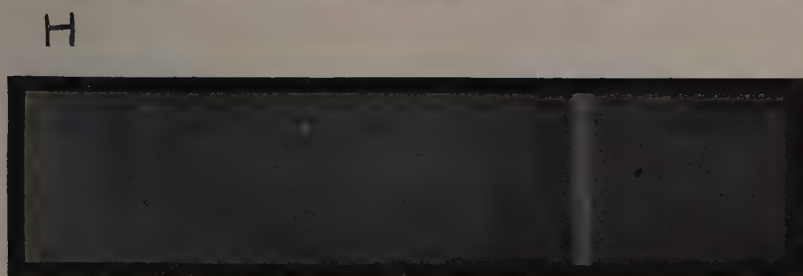
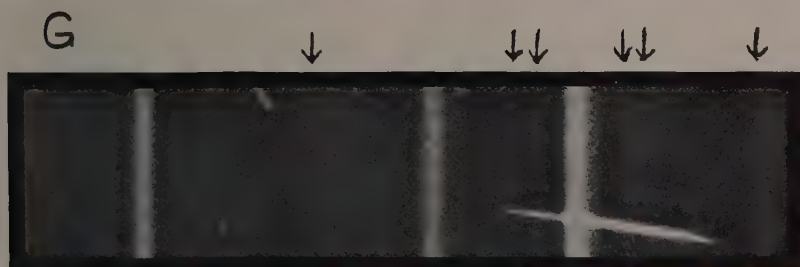
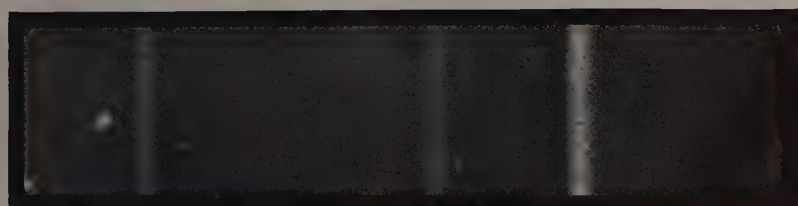
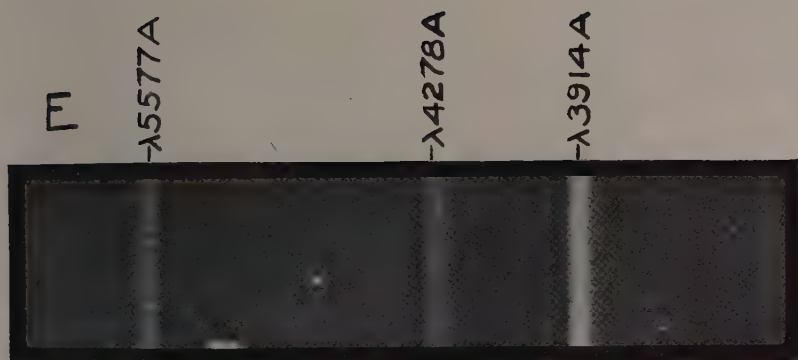
C



D



Spectrograms taken at Sulphur Mountain, Banff, Alberta, with exposures of 25, 30, 60 and 10 min., and slit widths of 0.2, 0.5, 0.05 and 1 mm. respectively.



Spectrograms taken at Sulphur Mountain, Banff, Alberta, with exposures of 15, 20, 30 and 5 min. respectively, and constant slit width of 1 mm.

NEW PHENOMENA IN X-RAY SCATTERING¹

By J. A. GRAY² AND W. H. ZINN³

Abstract

X-rays were scattered by a number of samples of graphite and charcoal in such a way that the scattering increased in intensity as the scattering angle approached zero. In certain cases the scattering at small angles was very similar to the scattering of α -particles; this result cannot be explained easily on the basis of the current views on the nature of X-rays and matter. Experiments are being devised to test what part adsorbed gases play in the phenomena, and to determine whether the scattering at very small angles is a true particle scattering.

Work carried out in this laboratory last session by Miss M. F. McDonald showed that artificial graphite scattered X-rays appreciably at small angles. Her observations led the authors to continue the work and thence to study the distribution of the X-radiation scattered by various samples of charcoal. The experimental arrangement was as follows. The primary beam defined by a set of parallel slits, fell on a radiator placed at the centre of a graduated circle. The scattered beam passed through a second set of slits to an electroscope where its intensity was measured. The position of these slits and the angle of scattering were read off the graduated circle.

The most interesting results have been obtained with a sample of blood charcoal, the intensity distribution curve for X-rays of average wave-length $0.7 \text{ \AA}$ being shown in Fig. 1, in which the intensity I_ϕ is plotted against the scattering

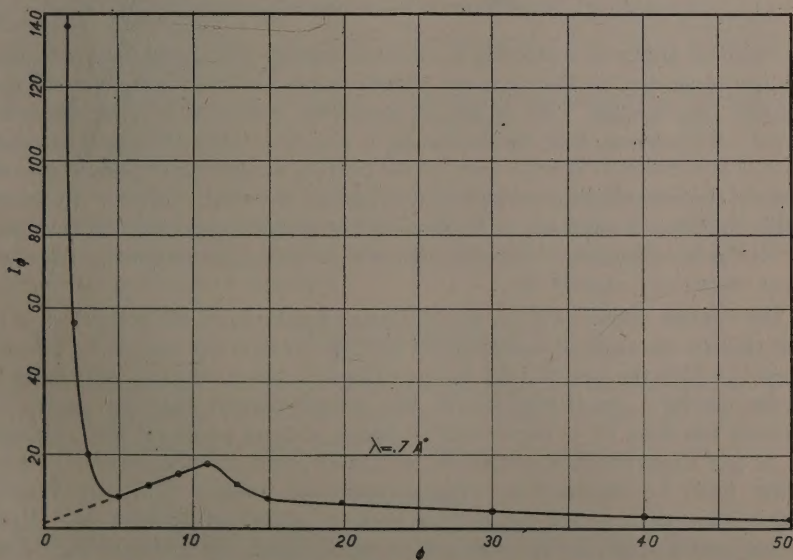


FIG. 1. Intensity distribution curve for X-rays of average wave-length $\lambda \ 0.7 \text{ \AA}$ (Blood charcoal).

¹ Manuscript received April 5, 1930.

Contribution from the Physical Laboratories of Queen's University, Kingston, Canada.

² Professor of Physics, Queen's University, Kingston.

³ Graduate student, and holder of a Studentship under the National Research Council.

angle ϕ . It will be noticed that the curve consists of two portions (a) a pronounced scattering at small angles, (b) a scattering similar to what would be expected from an amorphous substance.

Taking $I_\phi = 1$ when $\phi = 90^\circ$, it is found that $I_\phi = 75$ when $\phi = 1.5^\circ$, 27 when $\phi = 2^\circ$ and 9.5 when $\phi = 3^\circ$. To see how this small angle scattering varied with ϕ and the wave-length λ , the unfiltered X-rays from an iron target, have been used as primary rays; the average wave-length of the primary beam in this case being $1.9\text{\AA}$. The results are best shown perhaps by the numbers given in Table I, in which are given the relative values of ϕ , I_ϕ and $k\phi^{-4}$, where k is an arbitrary constant.

TABLE I
RELATIVE VALUES OF INTENSITY AND ANGLE OF SCATTERING

ϕ	I_ϕ	$k\phi^{-4}$	ϕ	I_ϕ	$k\phi^{-4}$
$0^\circ 36'$	56,000	56,000	$3^\circ 24'$	80	53
$0^\circ 52'$	14,000	12,900	$3^\circ 54'$	56	32
$1^\circ 6'$	5,000	4,900	$4^\circ 54'$	42	13
$1^\circ 36'$	1,040	1,100	$6^\circ 54'$	22	3
$1^\circ 51'$	620	620	$8^\circ 54'$	15	1
$2^\circ 6'$	350	370	$12^\circ 54'$	8	
$2^\circ 24'$	210	218	$29^\circ 54'$	11	
$2^\circ 54'$	120	103	$90^\circ 0'$	1	

With small angles of scattering I_ϕ varies so rapidly with ϕ that the probable error is a large one, so that it is not wished to lay too much emphasis on the empirical law, $I_\phi = k\phi^{-4}$, for angles of scattering less than 2° . It might be pointed out, however, that the scattering is similar to that of α -particles, and that it is possible that there is here a real particle scattering of X-rays due to centres of force distributed at random through the charcoal. It is not meant to suggest that the X-rays act as if they carried a charge; it may be that the effect is due to refraction of the rays near centres where the refractive index for X-rays varies very rapidly (1).

If the relative values of I_ϕ for the two wave-lengths used are compared, it is found that for an angle of scattering of 1.5° , $I_\phi = 1440$ in the case of $\lambda 1.9\text{\AA}$, as against $I_\phi = 75$ in the case of $\lambda 0.7\text{\AA}$; the value of I_ϕ being taken as unity in each case for $\phi = 90^\circ$. As $(1.9/0.7)^3 = 20$, this would suggest that for angles of scattering less than 2° , I_ϕ varied as λ^3 . Again, it must be stated that it is not easy to get these relative intensities accurately, and for the present, the λ^3 relation must be regarded as very approximate indeed. The two results together show that, within rather wide limits of experimental error, the blood charcoal used scatters X-rays intensely at small angles, the scattered radiation being given approximately by the formula $I_\phi = \lambda^3\phi^{-4}$.

Lately, through the kindness of Dr. E. J. Miller of Michigan State College, the authors have had the opportunity of examining other kinds of pure charcoal, which all showed marked scattering at small angles. None of them, however,

scattered in the same way that the blood charcoal did. The curves shown in Fig. 2 illustrate this. Curve A gives the scattering from blood charcoal for angles between $1^{\circ} 30'$ and 11° , curve B that from a sample of Merck's activated charcoal, which had been purified by Dr. Miller. Curve B may be divided provisionally into two parts, (a) a flat portion due possibly to gases adsorbed in pockets which have a random distribution, (b) a steep portion which at smaller angles may show that the scattering is similar to that previously found with the blood charcoal.

Experiments are now being devised to test the accuracy of these views and to show, in general, what part adsorbed gases play in the phenomena described above. A certain amount of work has been done in this connection, and slits are being constructed so that values of I_{ϕ} may be obtained for angles smaller than $36'$ of arc. It is thought that the results already obtained are sufficiently interesting to warrant their publication, although this publication is to be regarded as a preliminary one only.

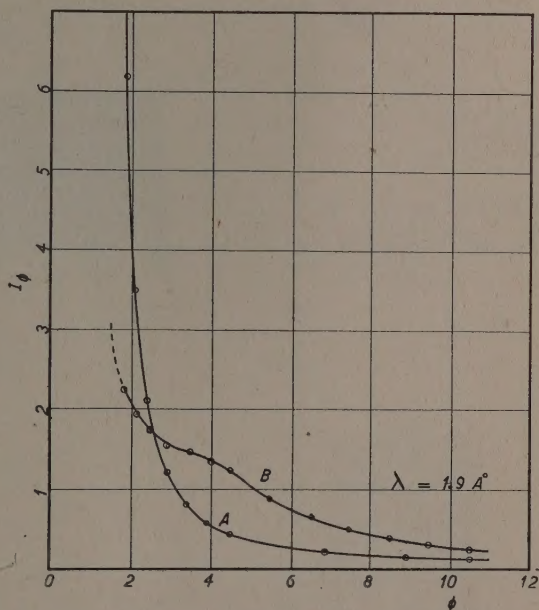


FIG. 2. Intensity distribution curve for X-rays of average wave-length $\lambda 1.9 \text{ \AA}$. (Curve A, blood charcoal, curve B, Merck's activated charcoal.)

Acknowledgment

The authors wish to express their thanks to Dr. J. A. McRae for advice about the properties of charcoal and to Dr. G. B. Frost and Dr. E. J. Miller for the gift of samples of very pure charcoals.

Reference

1. THOMSON, J. J. *Beyond the Electron*. Cambridge University Press, 1928.

